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No. 3

A Study of the Normal Constituents of the Potable Water of the San Francisco Peninsula

BY

JOHN PEARCE MITCHELL
Assistant Professor of Chemistry
Leland Stanford Junior University

WITH MAP

STANFORD UNIVERSITY, CALIFORNIA
PUBLISHED BY THE UNIVERSITY
1910

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PAPERS
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A STUDY OF THE NORMAL CONSTITUENTS OF THE POTABLE WATER OF THE SAN FRANCISCO PENINSULA

A knowledge of the normal constituents of natural water supplies is of especial importance in regions where the surface water is used extensively for drinking purposes, and where the population is increasing rapidly. The San Francisco peninsula is just such a region. Omitting altogether the consideration of the city of San Francisco itself, which draws its supply of potable water from many sources and from varying distances, the inhabitants of a large part of the peninsula depend upon streams, springs, and catchment reservoirs for their drinking water. At the same time the population is increasing so rapidly that in many places the present supplies are becoming inadequate. Even in the southeastern part of the peninsula, which is generously supplied with deep artesian water, the time when the present source will be overtaxed is not very distant. As a consequence of this increased tax on the supplies of water the danger of pollution will become greater; for with the increased population will come greater difficulty in finding streams with uninhabited watersheds, and with the increased draft on the wells will come greater danger of contamination from even distant sources of pollution. When these conditions have been realized, in order that a change for the worse may be recognized, and any threatened pollution guarded against, it will be of the utmost importance to know what were the normal constituents of the various supplies at a time when their purity was unquestioned. It was to furnish this needed knowledge that this study was undertaken.

The object in view has been to determine, for the region selected, just what are the normal constituents of the potable water supplies at different seasons of the year from the sanitary point of view, so that when in the future the purity of a certain supply is in question, data may be at hand which will be of fundamental importance in reaching a correct conclusion.*

* This investigation is an extension of the work done by Mr. Dane M. Greer, and presented in his thesis, entitled "A preliminary chemical survey of the waters of the eastern hydrographic basin of the San Francisco peninsula."

The considerations which have been outlined are not by any means restricted to this locality, but apply to the whole country. What has been done here on a small scale, should be done everywhere on a larger scale. In Massachusetts the State Board of Health did similar work for the whole state, and since then it has been done for other of the eastern states. In California nothing of this sort has been done systematically. The need however is just as great, and the opportunity offered by the large supplies of still clearly unpolluted water is greater, and it is to be hoped that the State will undertake the work while the results will still be of the greatest value.

When a water supply is considered chemically with the object of determining its potability, that is from the sanitary, and not from the industrial point of view, two points should be borne in mind. First, that a knowledge of every individual substance in the water is neither required nor possible to obtain. Second, that it is very seldom that the substances determined in the water themselves, but rather the pollution which their presence in abnormal quantities indicates, that renders it unfit for human consumption. In other words the chemical analysis simply indicates, by the abnormal character of the constituents, that a certain water is, or has been, exposed to pollution, and is therefore not safe for use as a drinking water unless the absence of disease carrying bacteria can be demonstrated. Furthermore, if the chemical analysis of a water indicates that it has been exposed to pollution in the past, and the bacteriological examination shows absence of immediate danger, the safety of the supply is in doubt, until such precautions are taken as will guard against infection in the future. It is then of importance to know the content of a water with regard to those particular constituents which signify pollution.

The constituents which are significant have been determined by experience. The most obvious of them is organic matter. No satisfactory method for determining directly the amount present is known, so that a number of indirect methods are in use. First the free ammonia is determined. Ammonia is known to be one of the final products of the decay of nitrogeneous organic matter, and an excessive amount of it in a water indicates that such decay is actually taking place. Next the so-called "albuminoid ammonia" is determined. This furnishes a measure of the nitrogeneous organic matter, the nitrogen of which is not yet completely converted into ammonia. Then the nitrites and the nitrates are determined. The former are an intermediate step in the oxidation of the organic matter by the "bacteria of nitrification," and their presence indicates this oxidation to be actually in progress; the latter are the final

products of this oxidation, and indicate the amount of organic matter which has been thus oxidized and not yet absorbed as food by living vegetable organisms. Two possible errors must be avoided in the consideration of the significance of the organic matter. One is that its absence may only indicate that it has decayed, been oxidized, and completely absorbed by plants, while the disease carrying bacteria introduced with it are still alive; and the other is that, though present in great quantity, it may be of purely vegetable origin and not necessarily injurious from a sanitary point of view.

Another determination sometimes made is that of the "oxygen consumed." This gives a measure of the amount of potassium permanganate which the water is able to reduce under certain conditions, and the amount is usually approximately proportioned to the "albuminoid ammonia" in the same water. The exact determination of this value is so largely dependent on the conditions under which it is made, and its significance differs so little from that of the "albuminoid ammonia," that it has not been included in this investigation.

A less direct indication of pollution is furnished by the chloride content of the water. Sewage contains large amounts of common salt; this salt is not affected by any of the processes of decay and subsequent oxidation of the organic matter, nor is it absorbed by plants; it is readily soluble, and once introduced is very sure to remain in the water until the latter is evaporated. Hence a very large salt content may indicate that at some time the water has been polluted. There is, however, one important fact which modifies this conclusion, and that is that there is a certain normal chloride content for every water supply. This normal content can be determined for a region, and then any excess of chlorides above the normal is significant. In Massachusetts the State Board of Health found that the normal chloride content varied with the distance from the Atlantic ocean, and was able to draw curves ("iso-chlors") on a map of the state which indicate the normal value in every locality. Similar work has been carried out in other states. The value of a chloride determination depends therefore on a knowledge of the normal value for the locality in question.

The hardness of a water, and the amount of residue left when it is evaporated, are also constituents which are generally determined. The hardness has more industrial than sanitary significance, but, since a drinking water is generally used for laundry purposes, it is a factor which comes within the scope of this investigation. The amount of residue left on evaporation serves as a check on the other determinations, and discloses any abnormal amount of inorganic matter present. Other

less important observations which are made systematically include the odor, color, turbidity, and sediment.

The interpretation of the results of an analysis is made difficult by the absence of any fixed standards of purity. Such factors as character of source, seasonal variation, topography of the region, climate, and the sanitary conditions of the immediate surroundings must all be considered. Thus the local conditions as well as the local standards must be known if the interpretation is to be of value. The furnishing of these local standards and their interpretation with reference to the topography, climatology, and sanitary condition of the locality, have been the main objects of this investigation.

This investigation covers the greater part of the San Francisco peninsula. On the eastern slope the northern boundary is given by a line extending west from Baden, not including the watershed of Lake Merced, and the southern boundary by the watershed between the Guadaloupe and Coyote rivers south of San Jose. On the western slope the boundaries are Salt Valley on the north, and the watershed between Pescadero and Butano creeks on the south. The area on the eastern side is about three hundred and eighty-five square miles, on the western two hundred and ninety, making a total of approximately six hundred and seventy-five square miles. The range of mountains which divides the peninsula into the eastern and western slopes varies in height from about six hundred feet at the northern boundary to about twenty-seven hundred feet at the southern. Parallel with this main ridge are numerous similar ridges of varying lengths and elevations. These are all the result of numerous, geologically recent, displacements. The main fault line of the San Francisco earthquake of 1906, traverses the peninsula from north to south in a direction approximately parallel to that of the main ridge. There is very little timber standing on the eastern slope of the mountains, the ground is largely covered with a heavy growth of shrubbery, the foot-hills are pasture lands, or are cultivated, and the floor of the valley is under cultivation as far as the marshes which border the bay. The western slope varies from pasture land at the northern end, to dense forests with a large amount of standing redwood timber near the southern boundary. The soil is largely loose or sandy, with considerable, irregular, beds of clay. On the east the land below the foothills is devoted to the raising of fruit, vegetables, hay and grain, while on the west the portion which is not wooded is used almost exclusively for pasture lands in connection with large dairies. A small strip along the ocean at the northern end of the western area is used for vegetable raising; mostly for artichokes, for which the climate seems peculiarly adapted.

The climate of the peninsula is typical of that of the central and southern California coast. There is a long dry season during the summer months, which is followed by light rains in the autumn, and then, during the winter, by a prolonged period of heavy rainfall. In the Santa Clara valley, that is on the eastern slope, the rainfall increases from San Jose at the southern end to San Francisco at the northern. Thus the mean annual rainfall at San Jose is 14.88 inches,* at Menlo Park 16.43 inches, at San Mateo 20.71 inches, and at San Francisco 23.00 inches. More than half of the annual rainfall occurs during the months of December, January, February and March. Rain during July and August is almost unknown. The annual rainfall, except in San Francisco, is very seldom less than ten inches, or more than twenty. A fair example of a normal year is given by the record obtained at Menlo Park in 1895. The precipitation by months was as follows:

Jan.	Feb.	Mch.	Apl.	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.	Total
7.12	1.59	2.30	1.44	0.36	0.00	0.00	0.00	0.00	1.16	1.45	1.13	—16.55

The wide variation in the rainfall within this comparatively small area is very marked. There are two small areas where the annual rainfall reaches fifty inches, one at Lake Pilarcitos near the northern boundary of the field of investigation, and the other at the head waters of Boulder and San Lorenzo creeks, south of Black Mountain, and just beyond the southern boundary of the field.† At San Mateo, where the peninsula is about ten miles wide, the annual rainfall is twenty inches. Westward it increases to the maximum of fifty inches at Lake Pilarcitos, and drops again to twenty inches at the ocean shore. At Palo Alto the mean annual rainfall is about sixteen inches, at Searsville reservior, only five miles westward, it is about thirty-five inches. In general the rainfall on the western slope is greater than that on the eastern; and that along the ridge is from two to three times that in the Santa Clara valley. The rainfall for the seasons during which this work was carried out was, for 1906-1907 20.77 inches, and for 1907-1908 12.14 inches at Palo Alto where the mean annual rainfall for twelve years is 15.87 inches.‡ The same relation between the rainfall for these seasons and the average value, which exists at Palo Alto, may be considered to apply throughout

* "Climatology of California," by A. G. McAdie: Bulletin L, U. S. Department of Agriculture, Weather Bureau.

† "Rain and Run-off near San Francisco, California," by C. E. Grunsky: Proc. Am. Soc. of Civil Eng. 34: 339 (April, 1908).

‡ These data were very kindly supplied by Mr. John A. Squire, Displayman U. S. Weather Bureau, at Palo Alto.

the whole region. It will be noted that the season 1906-1907 had a rainfall well above the average, and the season 1907-1908 one somewhat below.

The summer "trade winds" introduce another very important factor. These winds blow from the northwest throughout the summer months, day after day, with great regularity, and with considerable force. One result of this is seen in the very marked bending of the trees in exposed places towards the southeast. Another result is observed in the fog and spray carried off the ocean towards the land. These strong, dry winds, sweeping over an ocean covered with "white caps," and over an almost unbroken line of heavy surf, pick up the spray thrown into the air, evaporate the moisture, and carry the salty residue in the form of an impalpably fine dust. This dust is eventually deposited on the ground, particularly in the more exposed places, and adds especially to the chloride content of the neighboring streams.*

The fog conditions throughout the area are also peculiar. The daily "trade winds" during the summer often bring a heavy bank of fog off the ocean towards the land, whose progress is checked by the main ridge of the peninsula, and from which the eastern slope is well protected. Thus the two sides are exposed to very different climatic conditions. The influence of these factors on the normal chloride content of the waters will be considered more in detail after the data collected have been presented.

The population of the area outside of the towns and villages is very small. Most of the towns are located either along the shore of the ocean or of the bay. An estimate of the population in the mountainous part, that is on the watersheds of the streams, indicates that it does not exceed eight per square mile. This is an average value, for a large number of the watersheds are totally uninhabited.

This study has been confined almost entirely to surface waters; that is to streams, springs and catchment reservoirs. Some work has been done on the wells, but they have not been covered at all thoroughly as they belong in a class by themselves which it is planned to consider in a separate investigation. The great majority of the wells in this area are located on the floor of the valley in the southeastern region. In the foothills on the eastern slope there are some wells sunk near the beds of the streams, to tap the underground flow, but most of the inhabitants depend upon streams, springs, and catchment reservoirs. On the western

* The large amounts of salt which may be transported in this way have been mentioned by E. Dubois: Haarlem. Arch. Mus. Teyler (2) 10, IV: 461 [Chemical Abstracts 1907: 1528].

side of the mountains there are almost no wells except in the small towns close to the ocean where there are no available streams or springs.

The constituents of normal water supplies which are most significant from the sanitary point of view have been determined. These are the free and "albuminoid" ammonia, nitrites, nitrates, chlorides, hardness,—permanent and temporary,—total solids, change of residue on ignition, color, odor—in both the cold and the heated sample—turbidity, and sediment. In a number of cases the chlorides only were determined.

The waters examined have been classified with reference to their probable purity as determined by the author by a study of the topography of the neighborhood, and of the location of possible sources of pollution. The purposes of this investigation exclude at once all waters known to be polluted, and every effort was made to collect samples of the purest water obtainable. A few polluted waters were examined for the sake of comparing them with the unpolluted. The following classification is based entirely on the evidence obtained in the field, and is independent of the analysis.

Class A comprises waters of unquestionable purity.

Class B comprises those for which it was determined that a possible source of pollution was so remote as to be negligible.

Class C comprises those perhaps slightly polluted, but not sufficiently so to affect materially the analytical data.

Class D comprises those probably polluted sufficiently to have some effect on the analytical data.

Classes A and B are comparable, for all waters not clearly in the first class were graded "C" until evidence was obtained to prove that any possible source of pollution could, at that time, be neglected.

The samples were all collected by the writer personally and according to the directions given by the Massachusetts State Board of Health.* Glass-stoppered bottles of about two and a half liters capacity were used. Before use the bottles were rinsed thoroughly with dilute sulphuric acid, five times with distilled water, and, since the distilled water contained considerable free ammonia, twice with ammonia free water. The stopper was covered with two thicknesses of clean filter paper, then with a heavy cotton cloth, and the whole tied firmly into place. When the sample was collected the covering, which had been protected from dirt, was replaced. In the laboratory the covering was removed, the bottle washed off with distilled water, placed on its side with the mouth over a

* Ann. Rep. St. B. of H., 1890, pp. 520.

sink, the stopper removed, and the bottle rolled along the desk until the contents had rinsed the mouth thoroughly on all sides. The stopper was rinsed at the same time, replaced, and covered with a clean beaker.

When taking the sample the bottle was rinsed three times, filled and emptied once, and then filled with the exception of a small air space. The stopper was rinsed thoroughly in the water being sampled. The sample from streams was taken either below the surface in a pool, or, where the flow was too small, from a place where the water was running rapidly over a stone. If the stream was very small the sample was taken from a small waterfall in preference to using a dipper. The mouth of the bottle was kept below the surface and above the bottom, and was always pointed upstream away from the collector. As far as the roads permitted every stream was followed to its source, and no stream was classed as "A" unless its source had been thus inspected, or its watershed was known to be entirely uninhabited. The samples from springs were taken from below the surface of the pool, and the rinsings were poured well to one side. In ponds and reservoirs the bottle was held eight to twelve inches below the surface,—the latter distance whenever possible. The nitrogen content of the sample was always determined within forty-eight hours of the time of collection, and generally within twenty-four.

The chemical analyses were made by the writer personally according to the standard methods in general use. It was known from previous experience that the waters in the region contained large amounts of chlorides, and, since the usual phenol sulphonic acid method for determining nitrates was known to be affected by such conditions, a special study of the methods for determining nitrates was undertaken.

Certain of the physical characteristics of the waters were determined in the following manner.

The turbidity of the water was considered to be due to the solid matter remaining in suspension after the sample had stood for twelve hours in the laboratory. The solid matter which settled to the bottom of the bottle during that time was considered to be the sediment. Neither the turbidity nor the sediment were determined quantitatively. The degree of turbidity was expressed by the terms * "very slight," "slight," "distinct," and "decided;" and the amount of sediment by the terms "very slight," "slight," "considerable," and "heavy." As a matter of fact the great majority of the samples examined were free from any turbidity, and contained only a very slight sediment.

The color of the waters examined was not expressed with reference

* cf. "Air, Water and Food," Richards and Woodman, 1906 ed., 133.

to any standard, but was described as "brownish" or "yellowish" in the few cases where any appreciable tint could be detected.

The odor was determined for every sample before and after heating. The first test was made on the portion of the sample, about five hundred cubic centimeters, remaining in the sampling bottle after the other determinations had been made. The bottle was shaken thoroughly, the stopper removed and the odor determined at once. A beaker of about two hundred cubic centimeters capacity was then filled a third full of the water, covered with a well-fitting watch glass, and heated rapidly over a large burner. Just before the water boiled the beaker was put on the desk and allowed to cool for five minutes. The contents were then shaken with a rotary motion, and the nose put well into the beaker.* The different odors were described as "earthy," "vegetable," "musty," "mouldy," and "fishy," and their intensity as "very faint," "faint," "distinct," and "decided."

The Determination of the Nitrogen present as Free and "Albuminoid" Ammonia.

The first determinations made were those of the free and the "albuminoid" ammonia. The standard solutions and reagents were prepared according to the directions given by Richards and Woodman. † Distilling flasks of about two liters capacity, and condensers with water jackets from ninety to a hundred centimeters long were used. The method of procedure was to boil some water in a still, until fifty cubic centimeters of the distillate gave no color with the Nessler solution. A measured quantity, with few exceptions five hundred cubic centimeters, of the water under examination was then put in the flask, and the distillate collected in fifty cubic centimeter portions in Nessler tubes until the last portion was ammonia free. This gave the free ammonia. As the waters of the region were all strongly alkaline it was not necessary to add sodium carbonate to the distilling flask. Another portion of the water was put into an ammonia free still containing the alkaline potassium permanganate solution, and the distillate collected until the last portion was ammonia free. This gave the total ammonia. The difference between the total ammonia and the free ammonia gave the "albuminoid" ammonia. Usually five fifty cubic centimeter portions of the distillate were required for the free ammonia determination, and seven for the total.

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*cf. Richards and Woodman, loc. cit., 130-131.

†loc. cit.

The Determination of the Nitrogen present as Nitrite.

This determination was carried out by the regular method using sulphanilic acid and *a*-naphthylamine in acetic acid solutions. A blank determination on the distilled water used for rinsing was made with each set of determinations. One hundred cubic centimeter samples in Nessler tubes were used, and the tubes were allowed to stand in hot water for twenty minutes before comparing the colors.

The Determination of Nitrogen present as Nitrate.

The problem of the determination of the nitrogen which is present in a water in the form of a nitrate is one for the solution of which many methods have been suggested. Among them may be mentioned those of Schloesing,* Schloesing-Reichardt,† Schulz-Tiemann,‡ Crum-Lunge,§ Marx-Trommsdorff,|| Dewarda,¶ Busch** and Noll.††

All of these, however, apply only to the determination of relatively large amounts of nitrogen, and generally require the concentration of a rather large volume of water. This concentration is in itself objectionable, partly on account of the changes which may take place in the water during the concentration,‡‡ partly on account of the resulting delay, preventing the prompt analysis of the water, and lastly on account of the large sample which must be collected. Moreover many of the methods are tedious or complicated, and not at all suited for the routine analysis of a large number of samples.

There are, however, two methods which are not open to the above objections, and which have been extensively used for water analyses. They are known as the "Phenol-sulphonic acid" and the "Reduction" methods.

The Phenol-sulphonic acid method originated with Sprengel §§ and

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*J. f. pr. Chem. 62: 142 (1854).

† Zeit. anal. Chem. 9: 24 (1870).

‡ Berl. Ber. 6: 1041 (1873).

§ Phil. Mag. 30: 426. J. Chem. Soc. 21: 101. Berl. Ber. 11: 434.

|| Zeit. anal. Chem. 7: 412; 8: 364; 9: 171.

¶ Zeit. f. angew. Chem. 33: 113.

** Berl. Ber. 38: 861, 856, 4055.

†† Zeit. angew. Chem. 1901: 1316.

‡‡ cf. Tidy, J. Chem. Soc. 35, 53, 97, and A. H. Gill, J. Am. Chem. Soc. 16: 123 (1894).

§§ Pogg. Anal. 121, 188 (1864).

has been modified and investigated by Grandval and Lajoux,† Fox,‡ Johnson,§ Lindo,|| Rideal,¶ Smith,** Bartram,†† Hazen and Clark,‡‡ Gill,§§ and Andrews.||||

This method depends upon the formation of nitro-phenols by the action of phenol sulphonic acid on the nitrates left in the residue obtained by the evaporation of a known amount of the water under examination. The nitro phenols |||| formed are measured quantitatively by a colorimetric method based on the yellow color of the ammonium salts formed in the presence of an excess of ammonium hydroxide. It is well known that the presence of chlorides interferes with the accuracy of this method, and as the waters of the region covered in this investigation all contain large amounts of chlorides, it seemed essential to determine what results could be obtained by its application.

The details of the procedure adopted are as follows: Ten cubic centimeters of the water to be examined are measured with a pipette into a small, flat-bottomed evaporating dish placed on a water bath. The bath is so arranged that the dishes set well down into the steam.* The progress of the evaporation is watched; when less than one cubic centimeter is left, the dish is lifted with a pair of tongs and tipped about until the remaining liquid has wet the whole bottom of the dish; this is repeated frequently, and the last drop is evaporated in this way, and never on the water bath. If by oversight a determination is allowed to run to complete dryness on the water bath, it is rejected. When the residue is obtained, it is treated immediately with the required amount of the phenol sulphonic acid, the acid spread over the whole of the residue quickly by means of a small glass rod, and the dish set aside to cool. The contents are then diluted with water, rinsed into a Nessler tube, an excess of ammonium hydroxide is added. The volume is made up to 50 cubic centimeters with distilled water, and the color obtained compared with that of standard solutions.

The phenol sulphonic acid was prepared according to the directions

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† Compte Rendue 101: 62.

‡ Tech. Quart. 1: 54 (1887).

§ Chem. News 61: 15 (1890).

|| Chem. News 58: 1, 15, 28 (1888).

¶ Chem. News 60: 261 (1889).

** Analyst 10: 199 (1885).

†† Journ. Frank. Inst., March 17, 1891, referred to by Gill, J. Am. Chem. Soc. 16: 123.

‡‡ J. Anal. Appl. Chem. 5: 1, referred to by Gill, loc. cit.

§§ J. Am. Chem. Soc. 16: 122, 193.

|||| J. Am. Chem. Soc. 26: 388 (1904).

* A. H. Gill, J. Am. Chem. Soc. 16: 130 (1894).

given by Richards and Woodman;* phenol and pure concentrated sulphuric acid were mixed in the proportion of 3 g. of phenol to 37 g. of acid, and heated for six hours in a boiling water bath. A nearly colorless product was obtained.

Two standards were used. One was prepared by evaporating to dryness ten cubic centimeters of a solution of potassium nitrate containing 0.722 gram in one liter, using all the precautions above described, treating the residue with fifteen cubic centimeters of phenol sulphonic acid, and diluting to one liter. The strength of the solution was such that one cubic centimeter corresponded to 0.000001 gram of nitrogen present as nitrate. The second standard solution was prepared in the same way, but was ten times as strong. These solutions were used in all experiments on the various modifications of the method, so that all the results are expressed in terms of the same standards. They were found to give the same results a year after they were made up. The color given by the addition of ammonium hydroxide to ten cubic centimeters of the first solution, corresponded with that obtained with one cubic centimeter of the second solution.

The first experiment undertaken was to determine whether the color obtained by the evaporation of ten cubic centimeters of a solution containing a known amount of potassium nitrate, was the same as that of a corresponding amount of the standard solutions made as above. For this purpose a series of solutions containing known amounts of potassium nitrate were prepared, ten cubic centimeters of each evaporated and treated as has been described, and the color obtained read in terms of the standard solutions. The results obtained are given in Table I.

Observation of the standard solutions showed moreover that they kept their color without fading appreciably for two days.

The next experiments were designed to determine the influence of certain factors in the process of evaporation and treatment of the residues; namely the completeness of the evaporation, the interval between the removal of the dish from the water bath and the addition of the phenol sulphonic acid, the amount of phenol sulphonic acid added, the heating of the dishes after adding the acid, and the interval between the addition of the acid and the dilution with distilled water.

It was observed that in every case where one of two duplicate determinations was allowed to run to complete dryness on the water bath, loss of nitrogen resulted. Thus in one case two duplicate determinations on a solution containing 0.75 parts per million of nitrogen were made; one

* Richards and Woodman: Air, Water and Food, 2d ed., 241.

TABLE I.—TEST OF STANDARD SOLUTIONS.

Amount of N as KNO_3 in 10cc of solutions evaporated separately, expressed in parts per million	Feb. 2, 1907 Reading obtained in terms of standard solutions	Feb. 4, 1907 Repeated and obtained	Feb. 5, 1907 Repeated	Feb. 5, 1907 Repeated
0.01	0.01(?)	0.01(?)	....	
0.01	0.01(?)	....	....	
0.05	0.05	0.05	....	
0.05	0.04	0.04	....	
0.10	0.08	0.09	....	
0.10	0.09	0.09	....	
0.25	0.24	0.25	....	
0.25	0.23	....	....	
0.50	0.49	0.49	....	
0.50	0.49	0.49	....	
0.75	0.60	0.70	0.74	
0.75	0.60	....	....	
1.00	0.85	1.00	0.85	1.00
1.00	0.85	0.98	0.95	1.00
3.00	....	....	....	3.00
3.00	....	....	....	3.00
5.00	....	....	....	4.80
5.00	....	....	....	4.80

was allowed to evaporate completely and gave a reading by the standard solutions of 0.60, the other gave 0.70.*

A tendency toward loss of nitrogen was observed if the dishes were allowed to cool after being removed from the water bath and before adding the phenol sulphonic acid. This is illustrated by the following set of parallel determinations:

* cf. A. H. Gill, J. Am. Chem. Soc. 16: 130 (1894).

TABLE II. EFFECT OF COOLING BEFORE ADDITION OF ACID.

Phenol Sulphonic Acid added immediately on removal from water bath	Dishes allowed to cool after removal from water bath and before addition of acid
faint tinge	blank
faint tinge	blank
0.04	0.02
0.03	0.01
0.04	0.05
0.06	0.02
0.27	0.17
0.20	0.12
0.47	0.35
0.57	0.33
2.50	
2.20	1.60
3.50	3.00
4.00	3.50

Preliminary experiments indicated that loss of nitrogen could be prevented by the use of larger amounts of phenol sulphonic acid, but also that the color due to large amounts of the acid interfered with the delicacy of the method. This is shown in Table III. The tubes were compared with known amounts of the standard solutions, and the results expressed in parts per million. In order to reproduce more nearly the conditions existing in the case of an actual water analysis, known amounts of salt were also added to the solutions before evaporation.

From the data it will be seen that the use of as much as 3.5 cubic centimeters of the acid destroys the delicacy of the reaction, no color below that due to 0.10 parts per million of N could be read on account of the color due to the acid itself, and at the same time the results on the larger amounts are no better than those obtained with 1.5 cubic centimeters of acid. On the other hand the use of 1.5 cubic centimeters of acid gave better results than were obtained with ten drops of acid. Therefore, approximately 1.5 cubic centimeters was used in all the following experiments. When the ammonium hydroxide was added to this amount of acid the heat liberated was sufficient to raise the temperature appreciably,

TABLE III.—EFFECT OF AMOUNT OF PHENOL SULPHONIC ACID.

Parts per million of Nitrogen taken	10 drops P. S. acid 10 parts per mill. Cl.	3.5 cc P. S. acid 10 parts per mill. Cl.	10 drops P. S. acid 30 parts per mill. Cl.	1.5 cc P. S. acid 30 parts per mill. Cl.	3.5 cc P. S. acid 30 parts per mill. Cl.	3.5 cc P. S. acid 30 parts per mill. Cl.
0.01	tinge	....	tinge	tinge	2/14/07	2/16/07
0.01	tinge	....	tinge	....	....	....
0.05	0.05	....	0.04	0.03	....	....
0.05	0.05	....	0.03	0.05	....	....
0.10	0.08	0.10	0.04	0.06	0.10	0.10
0.10	0.08	0.10	0.06	0.06	0.10	0.10
0.50	0.30	0.40	0.27	0.30	0.35	0.40
0.50	0.32	0.45	0.20	0.35	0.40	....
1.00	0.75	0.90	0.47	0.90	0.80	0.85
1.00	....	0.85	0.57	0.85	0.85	0.80
3.00	3.00	3.00	2.50	2.30	2.00	2.00
3.00	....	3.00	2.20	2.30	2.70	2.70
5.00	4.50	4.70	3.50	3.70	4.50	4.00
5.00	4.70	4.70	4.00	4.00	4.50	4.00

and time for cooling was allowed before comparing the color with that of the standard solutions.

The heating of the dishes after the addition of the acid and before dilution was found to have no appreciable effect on the results. The data obtained are given in Table IV.

In the course of the work it was observed that those dishes which were allowed to stand a few minutes after the addition of the acid, and before dilution with water, tended to give higher results than did those where the acid was diluted at once. In the subsequent work the dishes were always set aside for a few minutes before the water was added.

The next point taken up was the interference of chlorides with the accuracy of the method. Determinations in solutions containing known nitrate and chloride content were carried out, the colors obtained being compared with those of the standard solutions as before. The data are given in Table V.

TABLE IV.—EFFECT OF HEAT AFTER ADDITION OF ACID.

Parts per million of N taken	1.5 cc of P. S. acid 30 parts per mill. Cl.	1.5 cc of P. S. acid. 30 parts per mill. of Cl. Dishes left on water bath 5 min. after addition of acid
0.01	tinge	tinge
0.01	....	tinge
0.05	0.03	0.03
0.05	0.05	0.02
0.10	0.06	0.06
0.10	0.06	0.05
0.50	0.30	0.35
0.50	0.35	0.30
1.00	0.90	0.70
1.00	0.85	0.80
3.00	2.30	2.70
3.00	2.30	
5.00	3.70	3.50
5.00	4.00	4.00

For quantities of nitrogen of one part per million or less the loss with 80 parts per million chloride is seen to be over 50 per cent. With higher nitrogen content the relative loss is less. With 30 parts per million of chloride the loss is about 30 per cent for quantities of nitrogen below one part per million, and still less above. With 10 parts per million chloride the loss is much smaller. It should be noted that the addition of such a large amount of chloride puts the method to a very severe test, but this is justified by the large chloride content of the waters of the region under examination.*

In actual analyses this loss of nitrogen due to the presence of chlorides might be overcome by using standard solutions prepared by adding known amounts of chloride to them before evaporation and treatment with phenol sulphonic acid. A solution was prepared in this way, exactly like the stronger of the two standard solutions described, except that an amount of sodium chloride corresponding to 30 parts per million was

* cf. Gill, loc. cit.

TABLE V.—EFFECT OF INCREASING CONCENTRATION OF CHLORIDES.

Amt. of P.S. acid	1.7 cc	1.7 cc	1.7 cc	1.7 cc
Parts per mill. of Cl.	0	10	30	80
Amount of N as Nitrate in solutions taken in parts per million				
0.01	tinge	tinge	tinge	tinge
0.01	tinge	tinge	tinge	tinge
0.05	0.04	0.04	0.03	0.02
0.05	0.05	0.04	0.02	0.02
0.10	0.09	0.09	0.06	0.05
0.10	0.09	0.08	0.05	0.05
0.50	0.45	0.30	0.30	0.20
0.50	0.45	0.30	0.25	0.20
1.00	0.90	0.75	0.60	0.55
1.00	0.90	0.60	0.60	0.50
3.00	3.00	2.50	2.50	2.00
3.00	3.00	2 70	2.50	1.00
5.00	5.00	4.50	4.00	3.50
5.00	5.00	4.50	4.50	3.50

added to the potassium nitrate solution before evaporation. In this case a well water containing about 30 parts per million chlorides and a small amount of nitrate was taken, and known amounts of potassium nitrate solution were added. The solutions obtained were compared with the standard made as above described, and also with the one used in the previous work. Three independent series were obtained; in the last two the amount of nitrate was measured by both the old and the new standard solutions. The data are given in Tables VI and VII.

All results are expressed in parts per million of nitrogen present as nitrate. In each series duplicate determinations were made at each concentration.

TABLE VI.—RESULTS WITH STANDARD NOT CONTAINING CHLORIDES.

Amount of KNO_3 added	Values Obtained with Old Standard Solution								
	First Series			Second Series			Third Series		
	Readings	Avg.	Diff.	Readings	Avg.	Diff.	Readings	Avg.	Diff.
none	0.4 0.3	0.35	....	0.3 0.2	0.25	....	0.4 0.4	0.4	....
0.5	0.7 0.6	0.65	0.30	0.5 0.6	0.55	0.30	0.70 0.70	0.70	0.30
1.0	0.8 0.7	0.75	0.40	0.8 0.85	0.825	0.575	0.9 0.9	0.90	0.50
5.0	4.0 4.0	4.0	3.65	3.8 3.6	3.7	3.45	4.0 4.0	4.0	3.60
20.0	16.8 16.8	16.8	16.45	16.8 16.8	16.8	16.55	18.4 18.4	18.40	18.0
50.0	48.0 46.4	47.2	46.85	46.4 46.4	46.4	46.15	48.0 48.0	48.00	47.60

The above data show, first, satisfactory agreement between the duplicates at each concentration. It was observed that, while with solutions of potassium nitrate in distilled water, especially when some chloride was also added, widely varying duplicates were sometimes obtained, with samples of natural waters the agreement was much better. Second, higher results were obtained with the new standard solution. Third, the agreement between the three independent series is fairly close. In the case of the stronger solutions the color produced was much too dark to be compared with the standards directly. In this case the solution was made up to 100 cubic centimeters with distilled water, thoroughly mixed by pouring back and forth between two Nessler tubes, and finally evenly divided between the tubes. That the division was equal was determined by comparing the color of the two tubes. This was repeated as often as necessary. In the case of the solution containing fifty parts per million of nitrogen the actual comparison was made in a tube containing one-sixteenth of the original solution. In this case this method of procedure

TABLE VII.—RESULTS WITH STANDARDS CONTAINING CHLORIDES.

VALUES OBTAINED WITH NEW STANDARD SOLUTION					
Second Series			Third Series		
Readings	Avg.	Diff.	Readings	Avg.	Diff.
0.4 0.3	0 35	.....	0.4 0.4	0.40	.....
0.6 0.7	0.65	0.30	0.80 0.80	0.80	0.40
0.9 0.95	0.925	0.575	1.0 1.0	1.0	0.60
4.4 4.2	4.3	3.95	4.6 4.6	4.6	4.20
18.4 18.4	18.4	18.05	19.2 19.2	19.2	18.80
49.6 49.6	49.6	49.25	52.8 52.8	52.8	52.40

gave better results than that obtained by using a smaller amount of water, as is shown by the following data:

TABLE VIII.

Evaporation of 10 cc gave:	Evaporation of 1 cc gave:
16.8	15.5
16.8	15.5
46.0	44.0
46.4	44.0

Mason* recommends that instead of using a standard solution as has been described, each standard comparison tube be prepared separately by the evaporation of known amounts of a standard potassium nitrate solution, to which an amount of sodium chloride corresponding to the chloride content of the water, as determined by

* Chemical Examination of Water, 3d ed., pp. 50-51. Jour. Am. Chem. Soc. 16:72 (1894).

previous analysis, has been added. This method was tried, and data obtained as shown in the following tables. In this case duplicates of each concentration of the water, to which known amounts of the nitrate solution had been added, were evaporated and treated in the regular way. The colors obtained were compared, first, with those of known amounts of the standard solution used in all the previous work, second with those of known amounts of the new standard solution to which thirty parts per million of chloride had been added, and, third, to those obtained by evaporating known amounts of the standard potassium nitrate solution, to which chloride corresponding to thirty parts per million had been added, and evaporated separately according to Mason's method. In this way standard tubes corresponding to concentrations of 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.4, 2.0, 2.3, 2.5 parts per million were prepared. In every case 10 cubic centimeters of the water was used. The first and second columns of this table are the same as those of the "third series" in the last table. The figures all refer to parts per million.

TABLE IX.—COMPARISON OF RESULTS WITH THREE DIFFERENTLY PREPARED STANDARDS.

Amount of KNO_3 added	I. Original Standard Solution			II. New Standard Solution with Chloride Added			III. Separate Evaporation of Standard Mason's Method		
	Readings	Avg.	Diff.	Readings	Avg.	Diff.	Readings	Avg.	Diff.
none	0.4 0.4	0.4	....	0.4 0.4	0.40	....	0.45 0.45	0.45	....
0.5	0.7 0.7	0.7	0.30	0.8 0.8	0.80	0.40	0.9 0.9	0.9	0.45
1.0	0.9 0.9	0.9	0.50	1.0 1.0	1.00	0.6	1.3 1.2	1.25	0.80
5.0	4.0 4.0	4.0	3.60	4.6 4.6	4.6	4.2	4.8 4.8	4.8	4.35
20.0	18.4 18.4	18.4	18.0	19.2 19.2	19.2	18.8	(21.6) (21.6)	(21.6)	(21.15)
50.0	48.0 48.0	48.0	47.60	52.8 52.8	52.8	52.4	(48.0) (48.0)	(48.0)	(47.55)

In the case of Mason's method at the high concentration, where the color had to be determined on a small fraction of the solution obtained, the tone of the color was found to differ so much from that of the standards, that the results obtained are very inaccurate.

To determine the constancy of the results obtained by Mason's method two more series of determinations were made. Each series is independent of the other, and in each case both Mason's standards and the standard solution containing thirty parts per million of chloride were used for comparison. To obviate the above mentioned difficulty due to the difference in the tone of the color in the case of the solutions of high nitrate content, only one cubic centimeter portions of the solution containing twenty parts per million of nitrate, and half a cubic centimeter of that containing fifty parts per million, were used. As a result direct comparison, with the standards, without any dilution, was possible. The results follow:

TABLE X.—SHOWING SUPERIORITY OF MASON'S STANDARDS.

Amount of KNO_3 added parts per million	Series A						Series B					
	Standard Solution			Mason's Standards			Standard Solution			Mason's Standards		
	Found	Avg.	Diff.	F'nd	Avg.	Diff.	Found	Avg.	Diff.	F'nd	Avg.	Diff.
none	0.30 0.20	0.25	....	0.50 0.40	0.45	....	0.30 0.30	0.30	....	0.40 0.40	0.40	....
0.5 0.5	0.50 0.60	0.55	0.30	0.85 0.95	0.90	0.45	0.60 0.50	0.55	0.25	1.0 0.9	0.95	0.55
1.0 1.0	0.70 0.80	0.75	0.50	1.30 1.40	1.35	0.90	0.70 0.70	0.70	0.40	1.30 1.30	1.30	0.90
5.0 5.0	3.80 3.60	3.70	3.45	5.00 5.20	5.10	4.65	3.80 3.80	3.80	3.50	5.20 5.20	5.20	4.80
20.0 20.0	18.40 19.20	18.80	18.55	2 00 2.00	2.00	19.55	20.00 19.00	19.50	19.20	2.00 2.00	20.00	19.45
50.0 50.0	48.00 48.00	48.00	47.75	2.5 2.5	2.50	49.55	48.00 48.00	48.00	47.70	2.5 2.5	2.50	49.45

In the following table the results are summed up. The known amounts of potassium nitrate added, and the amounts found are given for each series and by each method.

TABLE XI.—SUMMARY OF RESULTS SHOWING SUPERIORITY OF MASON'S STANDARDS.

Amount of KNO_3 added parts per million	Standard Solution				Mason's Method			
	I	II	III	Avg.	I	II	III	Avg.
0.5	0.40	0.30	0.25	0.32	0.45	0.45	0.55	0.48
1.0	0.60	0.50	0.40	0.50	0.80	0.90	0.90	0.87
5.0	4.20	3.45	3.50	3.72	4.35	4.65	4.80	4.60
20.0	18.80	18.55	19.20	18.85	(21.15)	19.55	19.45	19.50
50 0	52.40	47.75	47.70	49.28	(47.55)	49.55	49.45	49.50

From these data it appears that the standards prepared according to Mason's method give the best results that have been obtained. The method involves a preliminary determination of the chloride content of the water, and of the approximate amount of nitrate present, in order that the standards may be prepared correctly and over the proper range. One difficulty met with is that when as much as thirty parts per million of chloride is added to the standard solutions before evaporation, good agreement between the standards themselves is not obtained. The standards made up one day may not match those made up the next. Moreover the intensity of the color may not increase exactly with the increase in nitrate content. Thus in one case the 1.3 cubic centimeter tube had a lighter color than the 1.2 cubic centimeter and the 2.5 cubic centimeter tube was darker than the 2.7 cubic centimeter. These variations seem unavoidable in the case of high chloride content. Nevertheless, in spite of this source of error, this method gives the best results; that is, the error due to variations in the standards is less than that due to using any other system of standards.

The second method which has been studied is the so-called "reduction method," which depends on the reduction of the nitrogen present in the water as either nitrate or nitrite to ammonia, and the quantitative determination of the ammonia formed. Suitable correction must then be made for the nitrogen present as nitrite and as free ammonia. The process as a whole thus involves two distinct operations, namely the reduc-

tion of the nitrogen to ammonia, and the quantitative determination of the ammonia.

Since the accuracy of the method of reduction must be measured by the determination of the ammonia produced, the methods for accomplishing the latter will be considered first. There are three possible methods. The determination of the ammonia in a measured quantity of water, after reduction; by means of Nessler's reagent *directly*; the distillation of a measured quantity of the water, after reduction, and the determination of the ammonia in the distillate by means of Nessler's reagent; and finally the distillation of a measured quantity of the water, after reduction, into an excess of a standard acid solution, and titration of the residual acid with a standard alkali solution.

The first method, the direct Nesslerization of measured quantities of the water, after reduction, is the simplest.* The chief objections to it are that the process of reduction produces a slight turbidity and sediment, and that the addition of the strongly alkaline Nessler reagent, especially in very hard waters, produces a heavy precipitate. As a result the delicacy of the determination is seriously interfered with. Another difficulty met in the case of a water of high nitrate content is that, since all the ammonia must be determined at once, only a small portion of the water, after reduction (one cubic centimeter or less) can be used for direct Nesslerization without exceeding the maximum limit for comparison with the standard tubes. If a distillation method is used, a larger sample may be taken, the ammonia obtained in four or five portions of the distillate, and a larger quantity determined with accuracy. Actual trial showed that in every case the addition of the Nessler reagent produced a heavy, colored precipitate, and gave a *lemon* yellow tinge to the solution, so that accurate comparison with the standards was impossible.†

The second method for determining the ammonia, namely the distillation of a measured quantity of the water, after reduction, and the determination of the ammonia in the distillate with the Nessler reagent, is open to very few objections on the ground of inaccuracy. However, it is cumbersome, and time consuming. As carried out, the details are as follows: A large distilling flask, of about two liters capacity, is filled with a water containing very little ammonia, and the contents made strongly alkaline with sodium hydroxide. The flask is connected with a condenser exactly as in the determination of free ammonia. The con-

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* Hazen and Clark, J. Anal. Appl. Chem. 5: 3.

† A. H. Gill, J. Am. Chem. Soc. 16: 193 (1894).

tents of the flask are heated to boiling, and distillation continued until fifty cubic centimeters of the distillate give no reaction for ammonia with Nessler solution. The flask and contents are then allowed to cool for at least five minutes, and a measured quantity of the water under examination, after reduction, run into the flask from a pipette. The distillation is commenced at once, the distillate collected in Nessler tubes in fifty cubic centimeter portions, and the distillation continued until the last portion collected shows absence of ammonia when treated with the Nessler solution. The data given in the tables will show that good agreement between duplicate determinations was obtained. This method gave very satisfactory results, and was used in all the following determinations except where some other method is specified. By using several stills and running them at the same time that the free and albuminoid ammonia determinations were being made, the method required very little extra attention or time. Here again an objection rises in the case of waters of high nitrate content. The Nessler reagent method for the determination of ammonia is such a delicate one that the upper limit of its accuracy is soon reached. In other words the first portion of the distillate contains more ammonia than the highest of the comparison tubes. Thus in the case of a water containing twenty parts per million of nitrogen as nitrate, after reduction, ten cubic centimeters were put in the still, and the first fifty cubic centimeters of distillate contained ammonia corresponding to six cubic centimeters of the standard ammonium chloride solution. The darkest color which can be read at all accurately is that due to four cubic centimeters of the standard solution. In this case either less water may be put in the still, or the first portion of the distillate may be divided, but either alternative introduces a possibility of error.

To meet this objection the last method, namely the distillation into an excess of a standard acid solution and titration with standard alkali, was tried.

This method is not as delicate as the colorimetric method, and its usefulness would be confined to those cases where the nitrogen content is so high that only a very small quantity of the water could be used in applying the latter method. The results obtained are given below. The ammonia was distilled into an approximately N/50 sulphuric acid solution, and the excess of acid neutralized with a standard sodium hydroxide solution of about the same strength. Para nitro phenol was used as an indicator. Two independent sets of determinations were made. The results indicate that with very high nitrate content the ammonia had best be determined by distillation into standard acid.

TABLE XII.—DETERMINATION OF AMMONIA BY TWO METHODS.

Amt. of nitrogen in the water in parts per million	Found by distillation into standard acid		Found by Nessler method average of three determinations
	I	II	
20 00	18.18 18.30	19.75 19.25	18.87
50.00	44.93 43.31	43.70 42.91	43.71

A large number of methods for bringing about the reduction of the nitrate to ammonia have been suggested. Among them may be mentioned that of Foester, *—the reduction with metallic iron and potassium hydroxide in the presence of alcohol,—of Schmitt,†—the reduction with iron, zinc, and acetic acid,—of Ulsch,‡—the reduction with "ferrum reductum" and sulphuric acid,—and of Harrow,§—the reduction to nitrite in the presence of sulphanilic acid and *a*-naphthylamine. All these have given good results for relatively large amounts of nitrogen. The first three require the presence of the equivalent to half a gram of potassium nitrate, to obtain which it would be necessary to use one hundred cubic centimeters of a water containing seven hundred parts per million of nitrogen present as nitrate. The last method, Harrow's, is sensitive to only three tenths of a part per million.

Clearly none of these methods are applicable to the analysis of normal potable water without preliminary concentration,—the objections to which have already been mentioned. There are, however, two methods of bringing about the reduction which are sufficiently sensitive for the requirements of water analysis.

One by means of aluminium and caustic soda, and the other by means of the copper zinc couple in the presence of an excess of oxalic acid.||

* Given by Fricke, Analyst 16: 117. † Given by Fricke, Analyst 16: 117.

‡ Zeit. anal. Chem. 30: 175; 31: 392. § J. Chem. Soc. 1891: 320.

|| Tiemann und Gaertner in "Die chem. und bacteriologische Untersuchung des Wassers," Braunschweig, 1889: 208, 210, also give data obtained by the use of sodium amalgam as a reducing agent. The results were, however, very unsatisfactory.

The first of these, the reduction by means of aluminium and caustic soda, has given unsatisfactory results in the hands of other investigators.* The procedure adopted was to boil aluminium turnings in a small Erlenmeyer flask with weak sodium carbonate solution in order to drive out any free ammonia present. A measured amount of standard potassium nitrate solution was then added, also in some cases, in order to produce more nearly the conditions existing in the case of an actual water analysis, sodium chloride solution was introduced, and finally an excess of a sodium hydroxide solution which had been boiled till free from ammonia. The volume was then made up to twenty-five cubic centimeters with ammonia free water, and the flasks set aside over night. The next day the contents of each flask were rinsed with ammonia free water into a still, in which a weak sodium carbonate solution had been boiled until ammonia free, and the ammonia formed was distilled off and determined by Nesslerization of the distillate. Two blank determinations were made to test the purity of the reagents, and the average of the two values obtained was subtracted from each determination. The following table shows the unsatisfactory nature of the results obtained, all the figures referring to parts per million.

TABLE XIII.—RESULTS USING REDUCTION BY ALUMINIUM AND SODIUM HYDROXIDE.

Nitrogen added	No chlorides. Amount found	30 pts. per mill. Cl. Amount found	100 pts. per mill. Cl. Amount found	
blank	0.24	....	....	avg.
blank	....	....	0.20	2.20
0.20	0.14	0.10	0.06	
0.20	0.06	0.02	0.10	
1.00	0.10	0.50	0.22	
1.00	0.58	0.46	0.38	
5.00	1.26	0.90	1.10	
5.00	1.46	1.82	1.90	

Much more encouraging preliminary tests were obtained with the use of the copper-zinc couple as a reducing agent. Here the agreement obtained was good, in one case four duplicates on the same water gave

*cf. Hazen and Clark, A. H. Gill, Tiemans Gaertner, loc. cit.

respectively 0.36, 0.40, 0.45, and 0.45 parts per million of nitrogen present as nitrate. In a test on a water made up to contain 1.7 parts per million of nitrogen as nitrate, the average of two determinations was 1.35 parts per million; and on a water made up to contain 5.0 parts per million the average of two determinations in each of two distinct tests was 4.8 parts per million. This method was adopted as being the more promising of the two, and was applied to many waters in which the nitrates were also determined by the phenol sulphonic acid method. The data obtained are given in connection with the discussion of the relative value of the two methods. The method proved to be of the greatest value with waters in which the nitrate content was low and the chloride content high. Many waters showed absence of nitrates, proving that the manipulations involved in the method could be carried out without the introduction of ammonia as an impurity. As finally developed the details of the method were substantially those given by Cairns.* A wide-mouthed glass stoppered bottle of about one hundred and fifty cubic centimeters capacity was nearly filled with granulated zinc. The bottle was then filled with water and a few cubic centimeters of dilute hydrochloric acid (1:1) was added. The acid was allowed to act on the zinc for about five minutes so that a clean bright surface was obtained. Then the acid was poured out, the zinc thoroughly rinsed with distilled water, and then covered with a three per cent copper sulphate solution. The solution was left in contact with the zinc until an even and firmly adhering coating of copper was deposited. If the solution remains in contact with the zinc too long the coating of copper will not adhere properly. The copper sulphate solution was next poured off, and the zinc rinsed again with distilled water. Only freshly prepared zinc was used, and the same zinc was never used twice. When prepared, the bottle containing the zinc was thoroughly rinsed three times with the water to be analyzed, and then filled to within about a quarter of an inch of the stopper. About half a gram of crystallized, pure, ammonia free, oxalic acid was then added, the bottle thoroughly shaken, and set aside over night. The first sixty determinations were tested the next morning for the presence of nitrites, which would indicate incomplete reduction, but none were found. This test was then discontinued except in cases where the nitrate content was known to be very high, but even with a content of fifty parts per million nitrates were never found.

The effect of three factors was studied in detail, namely the presence of chlorides, the amount of oxalic acid used, and the time allowed for the

* Quantitative Analysis, 3d ed., p. 278.

reduction to take place.* To test the effect of the presence of chlorides duplicate determinations were made in a well water containing thirty-five parts per million of chlorine, and on a sample of the same water to which sodium chloride corresponding to one hundred parts per million had been added. In the first case 1.80 parts per million were found, and in the second 1.76 parts per million. The difference is within the limit of experimental error. To determine the effect of the amount of oxalic acid used three determinations were made. In one case 0.25 gram, in the second 0.50 gram, and in the third 1.00 gram of acid was used. The result in the first case was 1.32, in the second 1.28 and in the third 1.28 parts per million of nitrogen; the difference between the first and second of 0.04 parts per million is within the experimental error. It appeared, however, that on standing for some time the sample containing 0.25 gram of oxalic acid lost ammonia much faster than the others, so that the use of less than one half gram of oxalic acid per hundred and fifty cubic centimeters of water taken, does not seem to be wise. To test the effect of the time allowed for the reduction the following experiment was carried out. A large quantity, five hundred cubic centimeters, of a well water was treated with the copper-zinc couple and oxalic acid under exactly the conditions described above, and from time to time samples were withdrawn and the amomnia in them determined. The following table shows the results:

TABLE XIV.—RATE OF REDUCTION.

Time after addition of Oxalic acid Hours	Min.	Nitrogen found in parts per million
11	40	0.84
12	45	1.36
13	30	1.48
17	30	1.40
36	—	1.48
60	—	1.12

It appears, then, that the ammonia should be determined within fourteen to thirty-six hours after the oxalic acid has been added. The results obtained in determining the amount of acid to be used, indicate that with less acid the loss of ammonia is more rapid. Usually twenty-

* Tieman and Gaertner carried on the reduction at a temperature of 100° C. and obtained results much lower than those found when the reduction took place at lower temperatures.

five cubic centimeters of the water, after reduction, were used for the ammonia determinations by the distillation and Nesslerizing methods. In the case of very high nitrates ten cubic centimeters were used, and in extreme cases even less. At first pieces of sheet zinc were used instead of granulated zinc, in which case one hundred square centimeters of zinc surface were allowed for two hundred cubic centimeters of water, but the granulated zinc gave better results. This is shown in the first column of the following table. The same table also shows the results which can be obtained with this method on solutions of known nitrate content. The solutions were prepared by adding known amounts of a standard potassium nitrate solution to a well water which contained a small amount of nitrate. All the results are expressed in parts per million of nitrogen. Each column represents an independent series of determinations.

TABLE XV.—COMPARISON OF SHEET AND GRANULATED ZINC FOR REDUCTION.

Amount of KNO added				I			II			III		
	Using Sheet Zn			Using Granulated Zn			Using Granulated Zn			Using Granulated Zn		
	F'nd	Avg.	Diff.	Found	Avg.	Diff.	Found	Avg.	Diff.	Found	Avg.	Diff.
none	0.08 0.08	0.08	....	0.12 0.12	0.12	....	0.12 0.12	0.12	....	0.16 0.16	0.16	....
0.50	0.48 0.36	0.42	0.34	0.60 0.72 0.72	0.68	0.56	0.44 0.44	0.44	0.32	0.76 0.84	0.80	0.64
1.00	0.80	0.80	0.72	1.12 1.12	1.12	1.00	0.96 0.92	0.94	0.72	1.16 1.16	1.16	1.00
5.00	3.20 3.20	3.20	3.12	4.20 4.30 4.20	4.23	4.11	3.3 3.2 3.3 3.4	3.33	3.21	4.20 4.30	4.25	4.09
20.00	....	....	....	14.80 .... 14.00	14.40	13.84	17.5	17.50	17.18	17.40	17.40	17.14
50.00	....	....	....	37.00 43.00	40.00	39.44	36.10 36.50	36.25	35.93	40.00 38.0	39.00	38.84

TABLE XVI.—COMPARISON OF NESSLER AND TITRATION METHODS.

Using Granulated Zn					
Nessler Method		Titration Method		Titration Method	
Found	Avg.	Found	Avg.	Found	Avg.
4.60	4.60				
19.40	19.40	18.18 18.30	18.24	19.75 19.25	19.50
44.0	44.0	44.93 43 31	44.12	43.70 42.91	43.30

To compare the results which have been obtained by the phenol sulphonic acid and reduction methods, the data have been summarized in the following table. In the first column are given the average results obtained by the phenol sulphonic acid method using standards prepared according to Mason's modification. In the second column are the averages of the three best results obtained by the reduction method on the same solutions,—using the results obtained by the titration method for determining the ammonia at the two highest concentrations.

The solutions were prepared by adding known amounts of potassium nitrate to a well water, containing about thirty-five parts per million of chlorides and noting the difference in the amounts found. Only those differences are given. The figures all refer to parts per million.

TABLE XVII.—COMPARISON OF PHENOL SULPHONIC ACID AND REDUCTION METHODS.

Amount KNO_3 added	Phenol Sulphonic Acid method. Mason's standards	Reduction method. Copper Zinc couple
0.50	0.43	0.51
1.00	0.87	0.91
5.00	4.60	4.27
20.00	19.45	18.87
50.00	49.50	43.71

It appears, then, that for low nitrate content the reduction method gives the best results, while if the nitrogen present exceeds five parts per million the phenol sulphonic acid method is the better.

The two methods were tested in actual practice by analyzing a

number of waters by both methods. The results are given in the following table. Neither method was perfected at the time the data was obtained, but nevertheless the results are fairly indicative of their relative value. All the figures refer to parts per million.

TABLE XVIII.—COMPARISON OF REDUCTION AND PHENOL SULPHONIC ACID METHODS.

Laboratory number	Reduction method	Phenol Sulphonic Acid method	Chloride content
3	0.40	0.35	37.00
	0.45	0.40	
10	0.23	none	36.23
13	0.06	none	16.60
14	none	none	12.82
15	4.0	6.00	22.00
	4.2		
16	0.11	none	18.44
17	none	none	56.50
18	0.24	none	41.10
19	0.08	none	26.30
20	0.10	none	52.80
21	0.18	none	37.50
22	0.08	none	48.70
23	0.04	none	33.40
25	0.72	0.50	39.20
		0.53	
24	1.0	0.9	37.30
	1.3	0.9	
26	none	none	13.82
27	none	none	17.50
28	none	none	17.70
29	0.16	0.10	24.10
		0.15	
30	none	none	36.90
31	1.23	1.5	14.30
		2.0	
32	none	none	19.80
33	0.15	none	20.50
34	0.15	none	14.50
35	0.08	none	10.60
36	0.02	none	9.40
37	none	none	40.57
39	2.00	1.8	25.45
		1.6	
40	none	none	31.81
41	none	none	14.75
42	none	none	61.50
43	0.18	none	135.50
44	0.11	none	29.50

TABLE XVIII (CONTINUED).

Laboratory number	Reduction method	Phenol Sulphonic Acid method	Chloride content
45	0.26	none	42.41
46	0.72	0.3	42.41
47	2.04	2.0	30.40
		2.3	
48	none	none	79.20
49	0.12	none	27.70
50	0.04	none	27.85
51	0.10	none	37.15
52	0.16	0.25	38.26
		0.30	
53	0.14	0.20	45.92
		0.20	
54	none	none	37.43
55	0.11	none	37.53
68	0.19	0.25	24.25
80	0.46	0.35	173.89
82	0.30	0.25	20.80
		0.27	
84	0.84	0.78	14.75
97	2.44	2.30	30.89
98	1.60	1.70	26.55
99	0.44	0.47	27.84
100	0.36	0.40	26.18

The data given may be summarized as follows: Fifty-one waters were examined by both methods. Of these twelve gave no nitrate by either method. Twenty gave amounts of nitrate varying from 0.02 to 0.26 parts per million by the reduction method, and none at all by the phenol sulphonic acid method. The other nineteen gave nitrate by both methods. In no case was nitrate found by the phenol sulphonic method and not by the reduction method.

Of the twenty cases where nitrates were found by the reduction method and not by the phenol sulphonic acid method, fifteen gave amounts between 0.02 and 0.15 parts per million and five between 0.18 and 0.26 parts per million. In the group of fifteen the chlorides present ranged from 9.40 to 52.80 parts per million. In the group of five the chloride content varied from 36.23 to 135.50 parts per million. In no case was as much as 0.18 parts per million of nitrogen lost by the phenol sulphonic acid method in the presence of less than 36.23 parts per million of chlorides.

Of the nineteen cases where nitrates were found by both methods, in ten the reduction method gave the highest value, and in nine the

phenol sulphonic acid method. This result cannot be explained by variation in the chloride content, nor can it be said from these data that one method is better than the other for low or for high nitrate content. In the ten cases where the reduction method gave the highest result the average difference was 0.16 parts per million. In the nine cases where the highest result was obtained by the phenol sulphonic acid method, discarding No. 15, one of the first analyses and an extreme case due possibly to faulty analysis, the average difference was 0.13 parts per million.

From the data presented the following conclusions may be drawn. For waters containing large amounts of chlorides the nitrogen present as nitrate may best be determined by the "reduction method." If the result of the determination indicates a nitrogen content in excess of five parts per million, the determination should be repeated, using the phenol sulphonic acid method and standards prepared according to Mason's method. Neither method gives strictly quantitative results. The experience obtained in this investigation indicates that an error of ten per cent may be made in the case of low nitrates using the reduction method, while with very high nitrate content, twenty parts per million or over, the phenol sulphonic acid method gives results within three per cent of the theoretical.

One limitation to the application of the reduction method should be considered, and that is met in the case of sewage or water containing very large amounts of vegetable matter. In such cases Parvis and Courtland * have found that the reduction method gives larger quantities of ammonia than correspond to the nitrates and nitrites in the water. They conclude that the copper-zinc couple reduces more of the nitrogen present as organic matter to ammonia. Tiemann and Gaertner, in the case of solutions to which egg albumin and caramel have been added, conclude that the albumin gives too high a result, while the caramel retards the reduction. None of these results, however, interfere with the application of the method to normal, potable waters, and it may still be regarded as the best method available for normal waters of high chloride content.

The Determination of the Chlorides.

The chlorides were determined in one hundred cubic centimeter portions by the usual method of titration with silver nitrate solution in the presence of potassium chromate as an indicator. In a few extreme cases smaller amounts of the samples were used.

* Proc. Camb. Phil. Soc. 14: 441 (July 16).

The Determination of the Hardness and Total Solids.

Hehner's acid method was used in the determination of both the temporary and the permanent hardness. As determined by this method the temporary hardness is the same as the "alkalinity." Erythrosine in the presence of chloroform was used as an indicator. The results were expressed in terms of parts per million of calcium carbonate.

The total solids were determined by the evaporation of one hundred cubic centimeter samples in weighed platinum dishes. The dishes containing the residues were heated for an hour in an air bath at 105° C. After the first weighing the heating was repeated for half an hour, or until a constant weight was obtained. The change of the residue on ignition was determined by holding the platinum dishes in the flame of a burner. The blackening which resulted was described as "very slight," "slight," "distinct," "decided," "considerable," and "excessive." The loss in weight on ignition was not determined.

The analytical results obtained are presented in the Table XIX. Certain determinations, namely those concerning the turbidity, sediment, color, odor and change on ignition are omitted for the sake of conciseness. The results of these determinations are discussed on page 39.

The area under investigation has been subdivided into sections, with reference to the various watersheds, each subdivision consisting of the watersheds either of one stream with its tributaries, or of a group of small independent streams. The subdivisions are designated as "E" or "W" according to their location on the eastern or western slope of the main ridge, and are numbered from north to south. There are thirteen such subdivisions on each side. The exact boundaries of these subdivisions are indicated by broken lines on the accompanying map. This map shows also the streams and their main tributaries, the principal towns, and the location of each point of collection of a sample. These points are indicated by a circle, followed by a number which is the laboratory number of one sample collected at the indicated place. With the aid of this key number, the analyses of the other samples from the same place may be found in the table.

The table is arranged as follows: In the first column is given the number of the subdivision, thus "W.6" means the sixth division from the north on the western slope, and reference to the map will show that this is the area drained by "Frenchman's creek." The subdivisions are arranged in order according to their location from north to south on the eastern, and then on the western slopes. In the second column, headed

"class," is given first a letter indicating the classification of the water according to the system described on page 11, and then a symbol indicating whether the source be a stream, spring or catchment reservoir. "St." indicates a stream, "Sp." indicates a spring, and "R" indicates a catchment reservoir whether artificial or a natural pond. The third column gives the date of the analysis in month and year. The arrangement of the analyses in the table is uniformly in the order: fall—winter—spring. The fourth column contains the laboratory number of the analysis, and the other columns give the results of the analysis expressed in parts per million.

Discussion of Analytical Data.

The results of the determinations of turbidity, sediment, color, odor, and change on ignition were omitted from the table. They may be summarized as follows:

Most of the samples showed very slight or no turbidity. As a class the catchment reservoirs showed greater turbidity than did the streams. A few samples from streams collected after heavy rainfall showed marked turbidity. The samples bearing the following laboratory numbers showed turbidity graded "distinct" or "decided,"*—17, 49, 67, 75, 76, 82, 99, 111, 112, 114, 115, 116, and 185.

The sediment was generally very slight. Like the turbidity it was more marked in samples from catchment reservoirs than from streams, and was pronounced in those from streams after heavy rainfall. It was graded above "slight"* in the samples numbered 18, 19, 46, 75, 76, 82, 99, 115, and 185. Neither the sediment or the turbidity was found to have an appreciable effect on the more important constitutents.

The only samples where any appreciable color* was detected were the following: "very slight yellowish" in 27; "slight yellowish" in 11, 17, 18, 19, 20, and 30; "decided yellowish" in 10; "slight brownish" in 46, 49, 51, 82, 96, 98, 99, 103 and 161; "brownish" in 100, 111, 112, 115, 116, and 185.

The odor was determined in every sample before and after heating. In 72 samples, of which 15 samples were from deep wells, no odor could be detected. The most common odor was "vegetable" and next to it "earthy." The "vegetable" odor was most marked during the winter months, and the "earthy" during the fall months. In all 62 samples gave a "vegetable" odor, of which 23 gave less odor when heated, 27 gave more, and 12 showed no difference. An "earthy" odor was detected in

*cf. page 12.

TABLE XIX.—ANALYTICAL DATA FROM SURFACE WATERS.

Watershed	Class	Date	Laboratory Number	Ammonia Free	Ammonia Albuminoid	Nitrites	Nitrates	Chlorides	Hardness Total	Hardness Temporary	Hardness Permanent	Free Alk. Carbonates	Total Solids
E. 1.	B R	8/08	85.1	.....	.....	.....	.....	44.74	.....	.....	.....	.....	.....
		3/08	111	0.098	0.220	0.001	0.24	31.72	149.6	65.6	84.0	.....	170
		6/08	70.1	.....	.....	.....	.....	37.64	.....	.....	.....	.....	.....
	C R	3/08	45.1	.....	.....	.....	.....	23.97	.....	.....	.....	.....	.....
	D R	3/08	112	0.096	0.534	0.001	0.20	86.67	103.5	79.02	.....	24.48	325
E. 2.	A R	9/08	189	none	0.102	none	none	23.33	81.26	81.26	none	.....	140
		2/08	106	0.002	0.122	none	none	19.36	70.64	65.20	5.44	.....	130
		6/08	141	0.004	0.094	none	none	21.70	83.42	71.20	12.22	.....	130
E. 3.	B St	2/08	39.1	.....	.....	.....	.....	25.35	.....	.....	.....	.....	.....
	A St	9/08	92.1	.....	.....	.....	.....	25.15	.....	.....	.....	.....	.....
		2/08	41.1	.....	.....	.....	.....	19.36	.....	.....	.....	.....	.....
		6/08	62.1	.....	.....	.....	.....	19.98	.....	.....	.....	.....	.....
	A St	9/08	89.1	.....	.....	.....	.....	23.04	.....	.....	.....	.....	.....
	B R	8/07	19	0.008	0.242	none	none	26.3	119.8	96.4	.....	23.4	242
		2/08	102	0.010	0.130	0.0025	0.76	22.59	111.5	107.07	4.43	.....	188
		6/08	138	0.024	0.140	0.0005	0.44	25.36	120.7	120.7	none	.....	188
		9/08	186	0.100	0.248	none	none	26.30	130.73	122.4	8.33	.....	194
	D St	8/07	18	0.012	0.118	none	none	41.1	286.7	250.2	.....	36.5	412
E. 4.	B R	8/07	17	0.010	0.206	none	none	56.5	120.9	109.2	.....	11.7	290
	B Sp	9/07	31	0.022	0.052	0.003	1.7	14.3	177.7	164.0	13.7	.....	250
		2/08	84	none	0.070	0.002	0.84	14.75	148.65	131.0	17.65	.....	222
		5/08	131	0.012	0.030	0.0005	none	13.52	160.9	147.2	.....	13.7	235
E. 5.	A St	10/07	9.1	.....	.....	.....	.....	20.00	.....	.....	.....	.....	.....
		2/08	37.1	.....	.....	.....	.....	15.86	.....	.....	.....	.....	.....
		6/08	77.1	.....	.....	.....	.....	18.42	.....	.....	.....	.....	.....
	D St	10/07	8.1	.....	.....	.....	.....	30.15	.....	.....	.....	.....	.....
		2/08	36.1	.....	.....	.....	.....	22.22	.....	.....	.....	.....	.....
		6/08	76.1	.....	.....	.....	.....	33.60	.....	.....	.....	.....	.....
	D St	2/08	32.1	.....	.....	.....	.....	24.43	.....	.....	.....	.....	.....
	D St	9/07	2.2	.....	.....	.....	.....	63.6	.....	.....	.....	.....	.....
		2/08	30.1	.....	.....	.....	.....	18.9	.....	.....	.....	.....	.....
	A St	2/08	31.1	.....	.....	.....	.....	15.67	.....	.....	.....	.....	.....
	A St	8/08	172	none	0.028	none	none	24.38	243.5	204.2	.....	39.3	345
		2/08	83	0.006	0.048	none	none	12.91	128.5	115.0	13.5	.....	215

		5/08	132	none	0.008	none	none	19.68	213.6	200.7	.....	12.9	335
E. 5.	B R	9/07	32	0.008	0.070	none	none	19.8	106.2	97.9	.....	8.3	230
		2/08	85	0.030	0.116	0.007	none	19.82	146.68	141.8	4.88	.....	275
		5/08	130	0.020	0.060	none	none	20.3	129.7	127.5	.....	2.21	240
		8/08	173	none	0.160	none	none	24.0	116.9	97.5	.....	19.4	220
	B R	9/07	30	0.008	0.074	none	none	36.9	204.7	190.0	14.7	.....	377
		2/08	82	0.020	0.140	0.006	0.32	20.8	109.6	78.2	31.4	.....	257
		5/08	133	0.018	0.092	none	0.40	34.56	192.0	154.6	37.4	.....	360
	B St	8/07	10	0.008	0.054	none	none	36.23	469	212	257	.....	843
		1/08	68	0.050	0.054	0.003	0.24	24.25	293	117	176	.....	640
		3/08	114	0.044	0.092	0.005	0.76	15.67	203	109	93.5	.....	552
		5/08	137	0.004	0.056	none	none	26.60	255.9	163.3	92.6	.....	750
		6/08	170	none	0.100	none	0.12	32.16	293.7	205.6	88.1	.....	785
	C St	8/07	11	0.006	0.060	0.001	none	44.8	246	242.4	.....	3.6	429
		3/08	115	0.020	0.038	0.004	0.32	22.4	210	147.2	62.8	.....	420
		6/08	171	none	0.062	none	none	47.23	260.04	254.1	5.94	.....	450
	B St	3/08	117	0.012	0.018	none	none	15.58	100.88	4.08	96.8	.....	394
	A St	3/08	48.1	.....	.....	.....	.....	14.75	.....	.....	.....	.....	.....
	C St	9/07	2.1	.....	.....	.....	.....	41.5	.....	.....	.....	.....	.....
E. 5.	B R	1/08	67	0.032	0.236	none	none	9.77	46.4	37.5	8.9	.....	84
		5/08	136	0.004	0.112	none	0.24	9.03	37.9	37.9	none	.....	70
	C R	5/08	58.1	.....	.....	.....	.....	13.52	.....	.....	.....	.....	.....
	B Sp	5/08	59.1	.....	.....	.....	.....	14.40	.....	.....	.....	.....	.....
		9/08	88.1	.....	.....	.....	.....	13.92	.....	.....	.....	.....	.....
	B St	9/08	87.1	.....	.....	.....	.....	21.60	.....	.....	.....	.....	.....
		1/08	69	0.012	0.036	none	none	18.62	222.1	205.0	17.1	.....	284
		5/08	135	0.010	0.028	none	0.20	16.13	243.6	239.4	.....	4.25	315
	C St	8/07	12	0.005	0.037	0.002	none	35.04	230	217	.....	13	351
		1/08	66	0.010	0.038	none	none	25.35	223.7	204.0	19.7	.....	302
		5/08	134	0.010	0.022	none	none	23.32	231.8	231.8	none	.....	320
E. 6.	C Sp	8/07	15	0.008	0.064	0.110	6.0	22.0	160.1	126.8	33.3	.....	278
		3/08	116	0.018	0.060	0.008	6.4	14.38	138.1	103.8	34.3	.....	252
		6/08	78.1	.....	.....	.....	.....	25.92	.....	.....	.....	.....	.....
	C Sp	11/07	13.1	.....	.....	.....	.....	22.68	.....	.....	.....	.....	....
	B Sp	11/07	14.1	.....	.....	.....	.....	14.38	.....	.....	.....	.....	.....
	B Sp	11/07	16.1	.....	.....	.....	.....	28.21	.....	.....	.....	.....	....
	C Sp	11/07	21.1	.....	.....	.....	.....	23.00	.....	.....	.....	.....	.....

Watershed	Class	Date	Laboratory Number	Ammonia Free	Ammonia Albuminoid	Nitrites	Nitrates	Chlorides	Hardness Total	Hardness Temporary	Hardness Permanent	Free Alk. Carbonates	Total Solids
E. 7.	A St	8/07	16	0.009	0.033	none	none	18.44	247.2	227.2	.....	20.0	313
		3/08	113	0.008	0.006	none	0.44	15.20	219.2	192.0	.....	27.2	267
		6/08	169	none	0.030	none	none	18.05	254.1	254.1	none	.....	295
	A St	3/08	46.1	.....	.....	.....	.....	15.86	.....	.....	.....	.....	.....
		6/08	79.1	.....	.....	.....	.....	36.19	.....	.....	.....	.....	.....
	A St	3/08	47.1	.....	.....	.....	.....	10.42	.....	.....	.....	.....	.....
		6/08	80.1	.....	.....	.....	.....	20.45	.....	.....	.....	.....	.....
E. 8.	A St	8/07	13	0.006	0.037	none	none	16.60	238.2	234.5	.....	3.7	293
		1/08	78	0.004	0.010	0.001	none	16.04	227.3	218.8	8.5	.....	287
		5/08	128	none	0.018	none	0.28	16.41	205.7	202.5	.....	3.2	275
	A St	1/08	79	none	0.008	0.0005	none	15.67	241.0	226.0	15.0	.....	293
		5/08	55.1	.....	.....	.....	.....	16.90	.....	.....	.....	.....	.....
	A St	8/07	14	0.003	0.032	none	none	12.82	158.1	145.0	13.1	.....	214
		1/08	81	none	0.004	0.001	none	12.08	217.5	194.0	23.5	.....	267
		5/08	129	none	0.028	none	0.56	13.14	163.5	154.0	9.5	.....	200
	C St	1/08	29.1	.....	.....	.....	.....	16.78	.....	.....	.....	.....	.....
	C St	1/08	29.2	.....	.....	.....	.....	16.87	.....	.....	.....	.....	.....
	C St	1/08	29.3	.....	.....	.....	.....	18.35	.....	.....	.....	.....	.....
		5/08	56.1	.....	.....	.....	.....	20.74	.....	.....	.....	.....	.....
	D St	9/07	25.	0.030	0.094	0.006	0.72	39.2	283.5	265.0	18.5	.....	461
		5/08	57.1	.....	.....	.....	.....	31.98	.....	.....	.....	.....	.....
E. 9.	B St	9/07	26	0.004	0.018	none	none	13.82	233.5	225.4	.....	8.1	297
		4/08	119	0.014	0.006	none	0.16	14.49	211.65	202.3	9.35	.....	285
	A St	9/07	27	0.010	0.040	none	none	17.5	210.5	208.2	.....	2.3	295
		1/08	71	0.012	0.014	none	none	17.52	185.6	164.5	21.1	.....	285
		4/08	120	0.018	0.030	none	0.80	17.09	185.3	185.3	none	.....	283
	A St	9/07	1.1	.....	.....	.....	.....	15.68	.....	.....	.....	.....	.....
	A St	9/07	1.2	.....	.....	.....	.....	15.68	.....	.....	.....	.....	.....
	A St	9/07	1.3	.....	.....	.....	.....	15.70	.....	.....	.....	.....	.....
	A St	9/07	1.4	.....	.....	.....	.....	15.20	.....	.....	.....	.....	.....
	A St	9/07	1.5	.....	.....	.....	.....	14.76	.....	.....	.....	.....	.....
	A St	9/07	1.6	.....	.....	.....	.....	14.76	.....	.....	.....	.....	.....
	A St	9/07	1.7	.....	.....	.....	.....	15.68	.....	.....	.....	.....	.....
	A St	9/07	1.8	.....	.....	.....	.....	16.1	.....	.....	.....	.....	.....

	A St	9/07	1.9	.....	.....	.....	.....	17.05	.....	.....	.....	.....	.....
	C St	9/07	1.10	.....	.....	.....	.....	18.45	.....	.....	.....	.....	.....
	C St	9/07	1.11	.....	.....	.....	.....	18.52	.....	.....	.....	.....	.....
	A St	9/07	1.12	.....	.....	.....	.....	12.90	.....	.....	.....	.....	.....
	C St	9/07	1.13	.....	.....	.....	.....	16.12	.....	.....	.....	.....	.....
		1/08	28.1	.....	.....	.....	.....	16.78	.....	.....	.....	.....	.....
		4/08	50.1	.....	.....	.....	.....	16.90	.....	.....	.....	.....	.....
	A St	9/07	28	0.002	0.028	none	none	17.7	265.1	257.8	7.3	.....	368
		1/08	72	0.004	0.014	none	none	17.24	208.7	187.4	21.3	.....	308
		4/08	121	none	0.028	none	0.48	16.42	225.7	213.5	12.2	.....	313
	C St	9/07	1.14	.....	.....	.....	.....	18.00	.....	.....	.....	.....	.....
	B Sp	1/08	28.2	.....	.....	.....	.....	14.20	.....	.....	.....	.....	.....
		4/08	50.2	.....	.....	.....	.....	13.44	.....	.....	.....	.....	.....
	C St	9/07	1.15	.....	.....	.....	.....	23.5	.....	.....	.....	.....	.....
	C St	9/07	1.16	.....	.....	.....	.....	23.5	.....	.....	.....	.....	.....
	C St	9/07	1.17	.....	.....	.....	.....	22.1	.....	.....	.....	.....	.....
	C St	9/07	1.18	.....	.....	.....	.....	24.9	.....	.....	.....	.....	.....
		1/08	28.3	.....	.....	.....	.....	27.66	.....	.....	.....	.....	.....
		4/08	50.3	.....	.....	.....	.....	25.63	.....	.....	.....	.....	.....
	C St	9/07	29	0.002	0.044	none	0.16	24.1	254.9	254.9	none	.....	333
		1/08	73	0.010	0.016	none	0.12	23.79	227.5	202	25.5	.....	350
		4/08	122	0.008	0.012	none	0.32	21.12	231.07	222.4	8.67	.....	322
	C St	9/07	1.19	.....	.....	.....	.....	24.0	.....	.....	.....	.....	.....
E. 10.	C St	9/07	3.1	.....	.....	.....	.....	28.58	.....	.....	.....	.....	.....
E. 11.	A R	9/07	36	0.010	0.068	none	0.03	9.40	56.9	52.7	4.2	.....	106
		1/08	74	0.026	0.134	0.0005	0.12	9.22	62.2	46.6	15.6	.....	140
		6/08	142	0.030	0.124	none	none	9.70	50.34	46.6	3.74	.....	95
	B St	9/07	34	0.008	0.046	none	0.15	14.5	170.9	167.2	3.7	.....	255
		1/08	76	0.008	0.232	0.003	0.08	12.26	133.5	109.4	24.1	.....	670
		6/08	144	0.010	0.006	none	none	12.39	172.66	161.1	11.56	.....	261
	B St	9/07	35	0.002	0.032	none	0.08	10.6	116.2	109.8	6.4	.....	190
		1/08	75	0.012	0.112	0.002	0.12	11.71	128.1	104.2	23.9	.....	385
		6/08	143	0.012	0.014	none	0.60	10.56	122.74	113.9	8.84	.....	190
	A St	9/07	4.4	.....	.....	.....	.....	11.06	.....	.....	.....	.....	.....
	A St	9/07	4.3	.....	.....	.....	.....	10.14	.....	.....	.....	.....	.....
	B St	9/07	4.2	.....	.....	.....	.....	10.14	.....	.....	.....	.....	.....
	D St	9/07	4.1	.....	.....	.....	.....	32.27	.....	.....	.....	.....	.....

Watershed	Class	Date	Laboratory Number	Ammonia Free	Ammonia Albuminoid	Nitrites	Nitrates	Chlorides	Hardness Total	Hardness Temporary	Hardness Permanent	Free Alk. Carbonates	Total Solids
E. 11.	D St	9/07	33	0.012	0.044	none	0.15	20.5	161.6	156.8	4.8	.....	255
		6/08	64.1	.....	.....	.....	.....	18.11	.....	.....	.....	.....	.....
E. 12.	B St	8/08	176	none	0.018	none	none	13.92	203.66	192.1	11.56	.....	273
	C St	8/08	177	none	0.076	none	0.080	15.93	181.34	174.2	7.14	.....	260
		2/08	86	0.016	0.024	0.001	none	10.14	128.46	104.0	24.46	.....	217
		6/08	145	0.006	0.028	none	0.24	11.52	168.3	128.5	.....	39.8	265
	B St	8/08	81.1	.....	.....	.....	.....	12.19	.....	.....	.....	.....	.....
	B St	8/08	82.1	.....	.....	.....	.....	16.61	.....	.....	.....	.....	.....
		2/08	87	0.020	0.010	none	none	10.88	123.58	109.0	14.58	.....	163
		6/08	146	0.006	0.014	none	0.80	13.44	210.8	202.3	.....	8.5	280
	B St	2/08	33.1	.....	.....	.....	.....	10.42	.....	.....	.....	.....	.....
		6/08	65.1	.....	.....	.....	.....	14.60	.....	.....	.....	.....	.....
E. 13.	A St	8/08	178	none	0.028	none	0.12	12.48	212.66	209.6	3.06	.....	275
		2/08	88	none	0.020	none	none	8.67	118.75	108	10.75	.....	155
		6/08	147	0.006	0.016	none	0.24	9.60	176.5	173.3	.....	3.2	223
	C St	8/08	83.1	.....	.....	.....	.....	14.11	.....	.....	.....	.....	.....
		2/08	34.1	.....	.....	.....	.....	10.05	.....	.....	.....	.....	.....
		6/08	66.1	.....	.....	.....	.....	11.81	.....	.....	.....	.....	.....
	D St	8/08	179	none	0.052	none	none	34.94	353.04	313.6	39.44	.....	568
		2/08	89	0.012	0.020	0.001	none	10.42	138.05	124.0	14.05	.....	190
		6/08	148	none	0.026	none	0.48	22.55	272.8	253.8	.....	19.0	380
W. 1.	B St	6/08	154	none	0.258	none	0.52	53.0	141.4	137.8	.....	3.6	240
	B St	6/08	71.1	.....	.....	.....	.....	41.8	.....	.....	.....	.....	.....
	B Sp	8/08	182	none	0.022	none	0.44	62.02	116.1	81.1	35.0	.....	240
		6/08	155	none	0.022	none	0.28	56.3	103.57	85.17	18.40	.....	235
	B Sp	8/08	185	none	0.014	none	2.16	56.83	184.6	156.7	27.9	.....	365
W. 2.	A St	8/08	183	none	0.052	none	0.08	28.80	86.55	86.55	none	.....	248
		6/08	156	none	0.022	none	0.28	28.14	180.1	177.04	.....	3.06	235
	A St	8/08	184	none	0.012	none	0.44	22.37	69.02	69.02	none	.....	125
		6/08	157	none	0.014	none	0.56	21.80	69.8	65.04	.....	4.76	128
	B St	8/08	86.1	.....	.....	.....	.....	23.23	.....	.....	.....	.....	.....
		6/08	72.1	.....	.....	.....	.....	23.04	.....	.....	.....	.....	.....
W. 3.	A St	10/07	46	0.078	0.266	0.005	0.8	42.41	66.9	58.3	8.6	.....	227
		2/08	96	none	0.070	none	0.2	40.11	55.5	36.8	18.7	.....	165

		6/08	158	none	0.080	none	0.56	43.80	71.3	65.35	.....	5.95	175
	A St	9/07	39	0.006	0.076	0.001	2.0	25.45	59.8	43.2	16.6	.....	132
		2/08	98	0.008	0.050	none	1.6	26.55	56.4	37.7	18.7	.....	115
		6/08	159	none	0.018	0.0005	2.0	25.06	57.2	57.2	none	.....	130
	B Sp	10/07	47	0.002	0.074	none	2.1	30.4	64.8	48.7	16.1	.....	162
		2/08	97	none	0.044	none	2.4	30.89	67.5	43.4	24.1	.....	157
		6/08	160	none	none	none	2.7	30.4	63.6	60.54	.....	3.06	132
	D St	9/07	6.1	.....	.....	.....	.....	47.48	.....	.....	.....	.....	.....
	C St	9/07	7.1	.....	.....	.....	.....	40.11	.....	.....	.....	.....	...
		2/08	38.1	.....	.....	.....	.....	34.11	.....	.....	.....	.....	.....
		6/08	74.1	.....	.....	.....	.....	48.67	.....	.....	.....	.....	.....
W.4.	B St	9/07	40	none	0.112	none	none	31.81	91.9	69.6	22.3	.....	160
		2/08	99	none	0.080	0.0005	0.45	27.84	63.8	45.4	18.4	.....	155
		6/08	75.1	.....	.....	.....	.....	39.64	.....	.....	.....	.....	.....
W.5.	B St	10/07	48	none	0.118	none	none	79.2	152.7	128.4	24.3	.....	362
W.6.	B St	10/07	49	0.010	0.090	0.004	0.12	27.7	99.1	88.4	10.7	.....	232
		2/08	100	0.008	0.104	0.0005	0.16	26.18	75.4	56.4	19.0	.....	155
		6/08	161	0.004	0.052	0.002	none	27.84	92.5	87.4	.....	5.1	155
W.7.	A R	9/08	187	0.004	0.090	none	none	21.22	59.33	59.33	none	.....	105
		2/08	103	0.008	0.152	0.001	0.24	17.06	48.78	40.8	7.98	.....	115
		6/08	139	0.016	0.022	none	0.48	19.30	55.21	49.6	5.61	.....	110
	A St	9/08	90.1	.....	.....	.....	.....	24.58	.....	.....	.....	.....	.....
		2/08	104	none	0.054	0.0005	0.68	21.11	64.22	56.75	7.47	.....	133
		6/08	60.1	.....	.....	.....	.....	24.00	.....	.....	.....	.....	.....
	A R	9/08	188	0.006	0.082	0.001	none	27.98	112.03	109.31	2.72	.....	185
		2/08	105	0.020	0.064	0.002	0.20	18.44	133.94	125.10	8.84	.....	185
		6/08	140	0.018	0.034	none	0.64	26.20	119.65	108.6	11.05	.....	180
	A St	9/08	91.1	.....	.....	.....	.....	35.23	.....	.....	.....	.....	.....
		2/08	40.1	.....	.....	.....	.....	21.76	.....	.....	.....	.....	.....
		6/08	61.1	.....	.....	.....	.....	31.68	.....	.....	.....	.....	.....
	A St	9/07	37	0.002	0.024	none	none	40.57	213.1	202.9	10.2	.....	311
		2/08	101	0.012	0.076	0.0005	0.38	33.19	148.42	135.0	13.42	.....	265
		6/08	167	none	0.060	none	0.12	38.60	212.5	209.4	3.10	.....	322
	C St	9/07	5.1	.....	.....	.....	.....	39.65	.....	.....	.....	.....	.....
	A St	10/07	50	0.002	0.080	none	0.04	27.85	102.7	92.5	10.2	.....	205
	C St	10/07	11.1	.....	.....	.....	.....	36.51	.....	.....	.....	.....	.....
	D R	10/07	51	0.018	0.098	0.002	0.12	37.15	117.6	78.7	38.9	.....	273

Watershed	Class	Date	Laboratory Number	Ammonia Free	Ammonia Albuminoid	Nitrites	Nitrates	Chlorides	Hardness Total	Hardness Temporary	Hardness Permanent	Free Alk. Carbonates	Total Solids
W.7.	D St	10/07	45	0.016	0.108	0.001	0.28	42.41	307.4	274.7	32.7	.....	558
W.8.	A Sp	10/07	41	0.018	0.030	none	none	14.75	43.9	15.6	28.3	.....	128
		2/08	94	none	0.024	none	none	12.91	47.3	16.9	30.4	.....	112
		6/08	162	0.008	0.020	none	0.44	14.40	42.14	26.84	15.30	.....	120
	B St	10/07	44	0.016	0.118	0.001	0.12	29.5	258.7	252.8	5.9	.....	440
		6/08	165	none	0.048	0.0005	0.20	27.56	284.0	277.88	.....	6.12	403
	A St	6/08	166	none	0.022	none	0.16	21.52	264.4	216.6	47.8	.....	372
	C St	10/07	10.1	.....	.....	.....	.....	33.19	.....	.....	.....	.....	.....
W.9	C St	10/07	43.	0.014	0.160	0.002	0.20	135.5	323.4	255.9	67.5	.....	823
		6/08	164	0.030	0.102	0.003	0.16	120.0	337.6	272.0	65.6	.....	708
W.10.	B St	10/07	42	0.016	0.046	0.0005	none	61.5	224.8	219.4	.....	5.4	429
		2/08	95	0.004	0.052	0.0005	none	31.35	145.1	124.5	20.6	.....	250
		6/08	163	none	0.050	none	0.20	47.25	231.2	212.5	.....	18.7	363
W.11.	C Sp	8/08	84.1	.....	.....	.....	.....	12.48	.....	.....	.....	.....	.....
	A St	8/07	23	0.038	0.130	none	none	33.4	340.5	262.5	78.0	.....	620
		2/08	90	0.044	0.160	0.0005	0.40	20.28	230.6	155.2	75.4	.....	400
		5/08	127	0.008	0.024	0.0005	0.40	34.84	321.9	252.2	69.7	.....	600
	C St	8/07	22	0.042	0.056	none	0.08	48.7	290.2	241.0	49.2	.....	532
		2/08	35.1	.....	.....	.....	.....	23.97	.....	.....	.....	.....	.....
		5/08	54.1	.....	.....	.....	.....	46.2	.....	.....	.....	.....	.....
	C St	8/07	21	0.024	0.074	0.004	0.18	37.5	320.0	268.1	51.9	.....	616
		2/08	91	0.034	0.158	0.001	0.20	22.59	197.8	142.	55.8	.....	383
		5/08	123	0.008	0.046	0.004	0.52	30.36	322.6	266.0	56.6	.....	585
	C St	2/08	93	0.014	0.134	none	0.28	27.20	127.62	108.5	19.12	.....	275
		5/08	126	0.014	0.050	0.002	0.44	72.00	207.4	207.4	none	.....	445
W.13.	A St	8/08	180	0.010	0.052	none	none	50.20	237.09	224.0	13.09	.....	406
		6/08	149	none	0.054	none	0.16	37.22	215.5	212.4	3.1	.....	365
	B St	8/08	181	0.016	0.074	0.001	0.44	55.82	334.9	334.9	none	.....	545
		6/08	150	0.012	0.068	0.005	0.32	46.50	309.6	296.0	13.6	.....	490
	B St	8/07	20	0.016	0.058	none	0.10	52.8	243.4	243.4	none	.....	452
		2/08	92	0.008	0.050	none	none	21.67	100.36	94.2	6.16	.....	248
		5/08	51.1	.....	.....	.....	.....	41.50	.....	.....	.....	.....	.....
	B St	5/08	124	0.014	0.042	none	0.72	42.5	213.25	205.6	7.65	.....	385
	D St	5/08	53.1	.....	.....	.....	.....	49.9	.....	.....	.....	.....	.....

1	Well	2/07	3	.....	.....	.....	0.32	37.0	.....	.....	.....	.....	380
		2/07	4	.....	.....	.....	0.32	37.0	.....	.....	.....	.....	.....
		9/07	24	0.031	0.022	0.020	0.35	37.30	227.7	210.0	17.7	.....	376
		10/07	52	0.034	0.002	0.014	0.20	38.26	194.1	168.8	25.3	.....	370
		2/08	107	0.022	none	0.025	0.64	36.51	225.9	202.6	23.3	.....	374
		6/08	151	none	0.018	0.025	0.44	39.07	225.98	216.8	9.18	.....	370
		8/08	175	none	0.010	0.020	0.36	37.73	236.0	221.0	15.0	.....	375
2		10/07	53	0.180	0.080	0.0025	0.32	45.92	221.8	201.0	20.8	.....	390
		3/08	118	0.220	0.020	none	1.00	44.99	219.5	151.5	.....	68.0	885
		6/08	168	0.172	0.064	0.002	0.32	51.95	232.8	162.4	.....	70.4	392
		8/08	174	0.192	0.020	0.0035	0.16	57.60	233.2	168.9	.....	64.3	401
3		10/07	56	0.118	none	none	none	29.50	91.5	53.3	.....	38.2	300
4		10/07	57	0.208	0.008	none	none	22.04	196.8	161.0	.....	35.8	275
		2/08	43.1	.....	.....	.....	.....	17.52	.....	.....	.....	.....	.....
5		10/07	58	0.158	none	none	none	21.67	255.0	210.0	.....	44.8	264
		2/08	108	0.166	0.018	none	none	19.18	176.8	121.4	.....	55.4	270
6		10/07	59	0.028	0.034	0.002	0.16	21.21	168.0	143.6	.....	24.4	282
7		11/07	60	0.058	none	0.0005	none	22.31	202.0	181.1	.....	20.9	307
8		11/07	61	0.068	0.048	none	none	20.84	178.5	126.1	.....	52.4	276
		2/08	109	0.072	none	none	0.25	18.07	194.6	131.1	.....	63.5	285
		6/08	152	0.036	0.024	none	0.48	20.64	197.9	126.5	.....	71.4	280
9		11/07	62	none	none	0.007	0.48	23.14	233.4	222.0	11.4	.....	345
		2/08	110	none	0.006	0.010	0.84	17.89	243.0	235.4	7.60	.....	350
		6/08	153	none	none	0.0025	1.40	21.80	253.0	245.0	.....	8.00	353
10		11/07	63	0.048	0.018	none	none	17.52	151.2	75.8	.....	75.4	295
		2/08	44.1	.....	.....	.....	.....	15.40	.....	.....	.....	.....	.....
		6/08	69.1	.....	.....	.....	.....	17.57	.....	.....	.....	.....	.....
11		11/07	12.1	.....	.....	.....	.....	14.75	.....	.....	.....	.....	.....
12		11/07	64	0.228	none	none	none	27.38	223.2	77.2	.....	146.0	375
13		11/07	65	0.032	0.026	none	none	79.66	178.2	178.2	none	.....	418
14		2/08	42.1	.....	.....	.....	.....	22.04	.....	.....	.....	.....	.....
		6/08	68.1	.....	.....	.....	.....	22.28	.....	.....	.....	.....	.....
15		9/08	192	0.096	none	none	none	258.24	217.26	211.99	5.27	.....	688

31 samples, of which 20 gave less odor when heated, 8 more, and 3 showed no difference. The "earthy" odor, therefore, is generally decreased by heating. Samples numbered 19 and 106, both from catchment reservoirs, gave a distinct "fishy" odor when heated, and sample 133, also from a reservoir, gave a decided "fishy" odor when cold which was decreased by heating. The following exceptional odors were also noted: 22 gave cold, faint "musty," hot, none; 179 cold, faint "mouldy," hot, faint "mouldy"; 39 and 40 cold, faint "mouldy," hot, very faint "mouldy"; 51 cold, faint "mouldy," hot, distinct "mouldy." A study of the data leads to the conclusion that the streams generally have a faint "vegetable" odor which is especially marked during the winter months, an "earthy" odor in the fall is not uncommon, and absence of odor is most common in the spring. The water from the deep wells may have a faint "earthy" odor, but is generally odorless.

The blackening of the residue on ignition in the samples from streams was generally "very slight" or "slight."* Thus 4 samples showed "no" blackening, 29 "very slight," 33 "slight," 19 "distinct," 19 "decided," and 5 "considerable." The amount of blackening was somewhat greater during the winter and spring than during the summer and fall. This is to be expected, since the rains wash considerable quantities of animal and vegetable matter into the streams. The streams on the western slope gave somewhat greater amounts of blackening than those on the eastern, but the difference was not very marked. The Corte Madera Creek gave uniformly high results, which, together with the abnormally high total solids shown by the same samples, may be due to the fact that the bed of the stream was greatly disturbed by the earthquake of 1906. Extensive landslides along its banks completely choked the stream with vegetable and mineral debris; and in many places forced it to seek a new course. When the samples were taken sufficient time for the restoration of the normal condition of the stream bed had not elapsed.

The samples from springs showed either "slight" or "very slight" blackening. Those from catchment reservoirs showed generally "distinct" or "decided," and were highest during the fall months at the end of the dry season. Certain reservoirs gave uniformly somewhat higher results than others. The samples for the deep wells showed either "very slight" or "no" blackening.

In the further discussion of the analytical data the several substances determined will be taken up in the order in which they are given in the table. The streams, springs, and catchment reservoirs will be considered first, and the wells will be dealt with in a separate class.

* cf. page 38.

Free and Albuminoid Ammonia.

The amount of organic matter in the water of a stream is independent of the geographical location of the watershed, and of the wind and fog conditions, but is markedly influenced by the surrounding vegetation and the time of the year. On the eastern slope the free ammonia during the fall months varied from "none" to 0.010 parts per million. It was about the same in the northern part of the western slope, but higher in subdivisions W. 8 to W. 13. Here the highest content was 0.038 parts per million, and the average 0.022 parts per million. These divisions include the watersheds drained by the Purisima, Lobitos, Tunitas, San Gregorio and Pescadero creeks, and are the most heavily wooded of any in the area investigated. The ammonia content of these streams is at all seasons different from that of the streams whose watersheds are less heavily wooded. During the winter months the streams on the eastern side generally show a slight increase in free ammonia, reaching a maximum of 0.020 parts per million. The same is true on the west, except in divisions W. 11 and W. 13, where the increase is up to 0.044 parts per million. In the spring there is a general decrease in the free ammonia throughout the whole territory to less than the fall content. On the east the range is about the same, but the average lower; on the west, especially in divisions W. 8 to W. 13, the decrease is more marked, the maximum being 0.014 parts per million.

The following maximum values may be taken for class "A" and "B" streams. In the fall, generally 0.010 parts per million, in especially heavily wooded regions 0.040 parts per million. In the winter generally 0.020 parts per million, in especially heavily wooded regions 0.050 parts per million. In the spring generally lower than in the fall in individual cases with a maximum of 0.010 parts per million except in heavily wooded regions where the maximum may be 0.015 parts per million.

The amount of albuminoid ammonia varies differently from that of free ammonia. Thus on the eastern side during the fall months the content varies from 0.028 to 0.050 parts per million. On the western slope the amount is greater, varying from a maximum of 0.118 parts per million in the north to one of 0.130 parts per million in the southern, W. 8 to W. 13, heavily wooded districts. During the winter there is a general decrease on the eastern side to almost one third of the above values. On the northern part of the western slope this is less marked, and in divisions W. 8 to W. 13 the variation is reversed and there is an increase to a maximum of 0.160 parts per million. In these regions of

heavy forest growth the amount of vegetable matter washed into the streams by the rains evidently overbalances the effect of the consequent dilution of the stream. In the spring there is an increase in the albuminoid ammonia in the streams on the eastern side to a value below that for the fall months, while on the west there is a decrease to a similar value, which is evidently the result of the thorough washing of the stream beds, and the absence of any amount of decaying vegetable matter, such as leaves, along the banks of the streams.

The maximum values for streams of classes "A" and "B" on the eastern side are: in the fall 0.050 parts per million, in the winter 0.025 parts per million (except in such a special case as the Corte Madera Creek, which has been discussed on page 50), and in the spring 0.030 parts per million. On the western side the values are higher; in the fall the northern streams may contain as much as 0.118 parts per million, and the southern 0.130 parts per million. In the winter the streams draining the heavily wooded regions, such as W. 8 to W. 13, reach a maximum of 0.160 parts per million. In these latter districts the amounts in the spring do not exceed 0.070 parts per million.

Disregarding the seasons, it may be stated that a stream of pure water in this area may contain as high as 0.050 parts per million of free ammonia, and 0.160 parts per million of albuminoid ammonia.

The streams known to be somewhat polluted and classed as "D" contained amounts of albuminoid ammonia in excess of the normal values that have been given. This was especially true during the fall months. At this time the presence of an excessive amount of albuminoid ammonia is a good indication of pollution, but after the winter rains the determination loses much of its significance. Thus the maximum during the fall on the eastern slope was given as 0.050 parts per million. Some streams graded "D" gave the following values, 0.118, 0.094, and 0.052 parts per million. In only one of these cases was the free ammonia above the normal value. The streams graded "C" generally showed somewhat abnormal albuminoid ammonia content and very rarely a somewhat high value for the free ammonia. The tendency was to give high albuminoid ammonia in the fall, followed by less than the normal decrease during the winter, and high or average content in the spring.

The springs examined are too few in number to admit of any reliable conclusions being drawn. They all gave the largest amounts of ammonia in the fall, and the lowest (with one exception) in the spring. The maximum values were 0.022 parts per million of free ammonia, and 0.074 parts per million of albuminoid ammonia.

The reservoirs vary somewhat among themselves, depending on how well they are cared for. Thus, for example, the Crystal Springs Lake

reservoir in the fall of 1908 showed a very much higher content of organic matter than in the fall of 1907. At the same time the statement was published in the newspapers that the owners had allowed the lake to become very dirty through neglect of the usual removal of the plant growths along the shores. Such a factor as this would overbalance any ordinary seasonal variation, and make comparison between cared-for and uncared-for reservoirs impossible. The data collected justify the following statements. The free ammonia should not exceed 0.030 parts per million under normal conditions. It is lowest in the fall, reaches a maximum during the winter, and decreases again in the spring. In a clean reservoir the albuminoid ammonia should not exceed 0.150 parts per million at any time; if the vegetable growth is unchecked the value may reach 0.250 parts per million. It is lowest in the spring, higher in the fall, and reaches a maximum value during the winter. The time of this maximum is the natural result of the addition of the vegetable matter, such as leaves, etc., carried by the streams at this time of the year.

Nitrites.

Small amounts of nitrites may be found in the streams at any season of the year, and may be regarded as insignificant. The amount should, however, not exceed 0.003 parts per million in the winter, or 0.001 parts per million at other seasons. A larger amount requires either some explanation such as would be given by abnormally high ammonia or nitrate contents, or assurance from the character of the watershed that pollution is out of the question. Even this small amount of nitrite is very rarely found during the fall or spring months, but a trace varying from 0.0005 to 0.002 may be regarded almost as a normal constituent during the winter. Streams graded "C" and "D" gave as high as 0.005 parts per million at varying seasons of the year. The almost invariable presence of free ammonia indicates that the process of decay induced by the "bacteria of nitrification" is actually taking place, and therefore a small amount of nitrite, since it is one of the transition products of this decay, is to be expected. Experience has shown that this amount is generally too small for detection, so that the presence of any detectable amount of nitrite in a stream, during the spring or fall months, may rightly arouse a suspicion as to the purity of the water which should require that direct evidence to the contrary be produced.

The springs examined which by their location were the least exposed to pollution did not contain any nitrites at any time. Two others showed rather large amounts. One, E. 4., B. No. 31 in the table, contained at the same time rather large amounts of nitrates, and the other, E. 6, C. No. 15

in the table, was not free from the possibility of direct pollution and contained distinctly abnormal amounts of nitrates. On the other hand another spring, W. 3, B. No. 47 in the table, contained a large amount of nitrate, but no nitrite.

In the case of the reservoirs the data are much the same as those for the streams. A quantity as small as 0.001 parts per million may be found at any season, but very rarely in the fall or spring, and is insignificant. In the winter the amount may reach 0.006 parts per million. A quantity is excess of this latter value should arouse suspicion.

Nitrates.

The streams do not normally contain any appreciable amount of nitrates during the fall months. In a few cases streams classed "A" or "B" showed as high a nitrate content as 0.15 parts per million on the eastern side, and 0.50 parts per million on the western. During the winter and spring months nitrates generally appear in those streams which contain none in the fall, and increase in the others. With a single exception nitrates above 0.75 parts per million were not found in any stream classed "A" or "B" at any time. The single exception was a stream on the northern part of the western slope (W. 3, No. 39) which showed a content as high as 2.0 parts per million. A spring in the same valley gave 2.7 parts per million nitrates with low ammonia and no nitrites. Both of these waters are distinctly abnormal. The surrounding country is wild and uninhabited, so that pollution is out of the question. It is of the same character as that of W. 2, 4, and 5, none of which furnished a similar case. The explanation must be sought in some abnormal underground condition.

The normal values for nitrates may be stated thus: in the fall, none, sometimes 0.15, and very rarely 0.50 parts per million. A trace of nitrate is a normal constituent during the winter and spring months, but the amount should not exceed 0.75 parts per million, and generally does not exceed 0.50 parts per million. An amount in excess of 0.75 parts per million may rightly be regarded with suspicion. The reverse of this, that polluted water will contain more than 0.75 parts per million of nitrates, does not hold, for waters graded "C" and "D" very rarely showed any abnormality in the nitrate content.

No reliable conclusion can be drawn from the data on the springs. Some gave higher values than others for no apparent cause. More than 2.0 parts per million at any season should certainly be considered suspicious.

The data on the reservoirs are more satisfactory. Here the normal conditions are the same as those for streams, namely no nitrates in the fall, and an amount not exceeding 0.75 parts per million during the winter and spring. This absence of nitrates in the fall is the natural result of their absorption by growing vegetation, for during the rainless summer months the fresh supply from streams is either completely cut off or very much curtailed.

CHLORIDES.

The discussion of the data concerning the chlorides will necessitate the consideration of each watershed separately, with regard especially to the local meteorological conditions, before a summary of the results is attempted. One point, which is of pronounced and general application, may well be considered in advance, namely the seasonal variation. This factor is of great importance in this region. As has been mentioned* the climate is characterized by a long, rainless summer, during the greater part of which strong winds, the "trade winds," blow regularly day after day from the northwest, over the ocean, and towards the land. These winds very often carry with them a bank of heavy fog and spray, whose progress eastward is more or less checked by the ridge of mountains running the length of the peninsula. As a result the western slope is exposed to sea-wind and sea-fog conditions which are extreme in character. These winds sweep over the ridge of mountains, concentrating with a funnel-like effect in the lowest saddles,† and sometimes carry the fog with them, and spread it in a fan shaped bank over the upper part of those eastern watersheds which head near such a pass. Thus the eastern watersheds are unequally exposed to the effect of this sea fog. The warm air of the valley prevents the progress of the fog eastward to any great extent, and a low ground fog in the valley is almost unknown. More often a high fog collects over the valley during the night, but this is usually dispelled a few hours after sunrise. These wind and fog conditions are peculiar to the summer months.

At the same time the climate is characterized by a practically complete absence of rain. The very rare summer shower is so quickly absorbed by the dry ground and vegetation, that its effect may be neglected. This absence of rain causes a very marked shrinkage in the streams, amounting generally to the drying up of the greater part of their lower courses, and sometimes to their complete disappearance. The same

* Page 9.

† These saddles, and the resulting wind currents, are indicated on the map with small arrows.

cause effects considerable concentration of all the water, stream and catchment reservoir, with a consequent increase in the chloride content. In the fall, the first rain is generally absorbed in the ground, and has little or no effect on the streams and reservoirs. When the heavy winter rains come, they introduce two factors. The rinsing of the watersheds and stream beds, and the dilution of the streams and reservoirs. This rinsing effect is not shown by any of the data, in every case a drop in the chloride content indicates the preponderating influence of dilution. Here again a marked difference between the streams on the eastern and western slopes is noticed. On the eastern side the influences which have been described apply with full force, on the western they are modified. In general it is true that the western streams are larger, and more constant in their flow, than the eastern. The moisture carried to their watersheds by the fog which has been described, as well as the dense forest growth in the southern part of the area, both counteract the concentrating effect of the rainless summer months. Moreover in the heavily wooded regions the rain water runs off much more slowly, and the diluting effect is less marked. As a result of these factors a less pronounced difference in the chloride content of the western streams between fall and winter is to be expected, and was actually found to be the case. The above differentiation between the eastern and western streams is a general one to which there are a few exceptions. The southern part of the eastern slope resembles in character that of the western, and the data reflect this similarity. In the same way the northern part of the western slope approaches in character to that of the eastern and affords corresponding data.

In the spring, before the beginning of the "dry" season, the contents of all the waters examined are intermediate between those of the winter and fall. These peculiar climatic conditions, which are characteristic to a greater or less degree of the whole Pacific coast of California, should be borne in mind when these data are compared with those of Eastern states. In the latter, where there are no distinct "dry" and "rainy" seasons, the variation between fall and winter is very much less pronounced, and is probably negligible. This seasonal variation introduces a factor which makes the construction of "isochlors" in the usual sense of the word impossible; for in this climate they can only indicate an average value, which must be modified according to the season. At the same time the importance of the study of local conditions, and the establishment of local standards for all seasons is greatly emphasized.

The subdivisions will next be considered separately, beginning on the East and proceeding from North to South, and then dealing with those on the western slope in the same order.

Chloride Content of Each Subdivision.

E. 1.—The division E. 1 includes all the territory east of the main ridge from the northern boundary of the field of this investigation, at Baden station, southward to the watersheds of San Andreas Lake and San Mateo Creek. This large area contains no important streams, none that flow at a time other than immediately after a heavy rainfall. The main ridge is low at the northern end, approximately 700 feet high, and the trade wind sweeps over it with almost unchecked force.

The ground is broken into irregular rolling hills and valleys, all exposed to wind and fog. Among these hills are a number of small ponds which are fed partly by rain water and partly by springs. The surrounding fields are used for the pasturage of cattle in connection with several dairies. High chlorides and high organic matter would therefore be expected in the pond waters. The data collected confirm this inference. One of the largest ponds showed chlorides amounting in parts per million to 44.74 in the fall, 31.72 in the winter, and 37.64 in the spring. Two smaller ones gave in the spring 86.67 and 23.97 respectively. The former gave evidence of pollution and was graded "D," the latter was simply an accumulation of rain-water, and dried up early in the summer. The significant data are those given for the large pond, which show an average chloride content of 38.03 parts per million.

E. 2—The division E. 2 includes San Andreas Lake and the surrounding hills whose streams drain into it. This lake is formed artificially by a dam at the southern end which impounds the water of a stream originally flowing towards the southeast. The resulting valley is protected on the west by the main ridge, which reaches an altitude of 1000 feet, but is exposed to the winds from the northwest. During the summer the trade wind sweeps through the valley with considerable violence, and carries with it some fog and spray. In addition to the waters flowing naturally into it, the lake is supplied through artificial flumes and tunnels with water from Lake Pilarcitos and from Stone Dam, both in W. 7. It is drawn upon continually as a part of the San Francisco water supply system. The chlorides found were in parts per million in the fall 23.33, in the winter 19.36, and in the spring 21.70. The average value is 21.46 parts per million. The average of the added water for Lake Pilarcitos is 19.19 parts per million, and of the much smaller volume from the Stone Dam is 24.21 parts per million. The average value for San Andreas, which is lower than those to the south as well as to the north of it, must be considered as accounted for, at least in great part, by this dilution with water of relatively low chloride content.

E. 3—The division E. 3 includes the watersheds and tributaries of San Mateo Creek. This stream rises in the hills to the west of E. 2, and originally flowed southeastward to a point, southwest of San Mateo, where a break in the chain of low hills between its course and the bay afforded an outlet northeastward. At this pass in the hills a very large dam was constructed in connection with the San Francisco water supply system, which resulted in the formation of Crystal Springs Lake. This latter is now a narrow, deep body of water some five miles long. It is supplied by San Mateo Creek and another small stream flowing from the north, by large amounts of rain water from the extensive watersheds to the north, west, and south, and by springs along its bottom. An inspection of the map will show the striking alignment of the San Bruno pond, San Andreas Lake, Crystal Springs Lake, Searsville Lake, and the ponds along the Los Trancos ridge, all following an old fault line which is now characterized by a large number of springs along its whole length. The northern two-thirds of the watershed is rigidly patrolled by the owners, and, with the exception of a few negligible keepers' houses, is absolutely uninhabited. To the southwest the watershed is crossed by three county roads, one of them much travelled, and along which a number of ranches are located. Pollution from these sources is not impossible, but the probability is so remote as to be negligible, especially when the long storage of the water in the lake is taken into account. Although the mountains to the west reach an altitude of a thousand feet, the valley is nevertheless exposed to the winds from the northwest. The greater distance from the ocean, as well as the better protection given by the mountains, lessen materially the amount of fog and spray carried with the wind. On the western boundary of the watershed and near the southern end, there is one of the saddles (altitude about 800 feet) which have been referred to.* The ocean to the west approaches the ridge at this point (Half-Moon Bay) and the winds sweep up the valley formed by Pilarcitos Creek, and through this pass, with considerable violence.

Chloride determinations were made in this division with the following results: On San Mateo Creek, some three miles above the inflow into the lake, a small seasonal variation with an average content of 21.50 parts per million was found. A mile further down, in the spring, 23.04 parts per million; on the tributary to the east, a stream dry from late spring to winter, 25.35 parts per million were found after a heavy rainfall. In the lake itself, near the dam and the intake of the pipe line, the amounts in parts per million were, in the fall 26.30, in the winter 22.59, in the spring 25.36, in the fall again 26.30. The average is 25.14 parts per million. A sample from the creek below the dam, carrying the drainage from the keeper's house, barns, etc., gave in the fall 41.1 parts per million.

* Page 53.

E. 4—Division E. 4 consists of the region between the foothills and the bay from Belmont to Menlo Park. It contains no streams that carry more than rain water during the winter, a catchment reservoir at Belmont, and a number of springs in the foothills. The reservior at Belmont is somewhat exposed to pollution from the ranches on the watershed. It was sampled once, in the fall, and showed a chloride content 56.5 parts per million. A spring in the hills southeast of Redwood City, located in a cattle pasture and inadequately protected, gave a small seasonal variation and an average of 14.19 parts per million.

E. 5—The division E. 5 is one of the largest, and has the most complex drainage system, of any in the territory under investigation. The length along the main ridge is some eleven miles, the width between the ridge and the foothills is from three to four miles. The height of the ridge increases from 2200 feet at the northern end to a maximum of 2555 feet at the southern; a little further south is Black Mountain with an elevation of 2787 feet. Along this ridge there are three saddles: One with an elevation of about 2000 feet at the northern end, at what is locally known as King's Mountain House; a second, very near the middle, with an elevation of 1680 feet; and the third at the southern end, with an elevation of about 2000 feet, and located between two peaks of 2555 and 2787 feet elevation respectively. The ocean winds sweep over the land west of the ridge with unbroken force, and are concentrated, funnel-fashion, at each of these saddles. At these points the fog and spray are carried over the ridge line, and spread out, over the upper parts of the neighboring watersheds. During the summer months this fog condition is of almost daily occurrence, and must be considered as an important factor in influencing the chloride contents of the adjacent streams.

There are three distinct streams in this division, each with a number of tributaries, and all flowing eventually into the San Francisquito Creek and hence into the bay. The middle system consists of the Corte Madera Creek, its tributaries, and the small mountain streams as far northward as Bear Creek. All these streams flow together at Searsville, where a large dam impounds them. At the height of the rainy season a large amount of water flows over the dam, otherwise the only outlet is through the pipes of the Stanford University water system. North of this system Bear Creek, West Union Creek, and a few small tributaries first unite and then join the San Francisquito Creek just below the Searsville dam. The largest of these, and the only one that generally flows throughout the year, is Bear Creek, but the greater part of its water is collected by a dam near the point where the stream enters the valley, and is diverted

through a pipe line into an artificial reservoir known as "Bear Gulch" or "Menlo" reservoir. A small amount of water flows down the upper part of the West Union Creek channel during the greater part of the year. The third, southern, system is composed of Los Trancos Creek and its tributaries, and enters San Francisquito Creek about two and a half miles below the Searsville dam.

The watershed of the northern, Bear Creek, system is exposed to the ocean winds coming through the saddle at King's Mountain House. Samples from a good sized stream, unquestionablely pure, showed a normal seasonal variation and an average value of 18.09 parts per million of chlorides. Another mountain stream, sample in the winter, gave 15.67 parts per million. Bear Creek, at the diverting dam, gave an average of 18.99 parts per million. In the "Bear Gulch" reservoir the average was 20.04 parts per million. West Union Creek, known to be somewhat polluted, gave an average of 28.66 parts per million. Just above its junction with San Francisquito Creek the chlorides in the fall were 63.6 parts per million, and after heavy rains the more normal value of 18.9 parts per million.

The abnormal conditions existing in the bed of Corte Madera Creek have been described on page 50. In the upper part of the stream the average was 26.98 and from the lower, below possible sources of pollution, it was 38.14 parts per million. Two small streams well up on the watershed gave, in the winter, values of 15.58 and 14.75 parts per million, and down in the valley below several ranches, the main stream showed, in the fall, 41.5 parts per million. This watershed is exposed to the effects of the southern saddle described on 57. The fog appeared to cross the ridge at this point as often, if not more often, than at any other point. In Searsville Lake the average chloride content was 30.75 parts per million.

The Los Trancos watershed is somewhat less exposed, as it is separated by a ridge of Black Mountain from this southern saddle. Along this ridge are located a number of ponds, whose position in a line with Searsville, Crystal Springs, and San Andreas lakes has been noted on page 56. The largest of these ponds gave an average chloride content in the winter and spring of only 9.40 parts per million; another, in the spring, 13.52; a small stream flowing from a spring nearby, an average of 14.16 parts per million. The creek itself, above possible pollution gave an average value of 18.78, and below possible pollution, 27.90 parts per million.

E. 6—The subdivision E. 6 is a small, hilly area, drained by Madera Creek. The stream is dry in the late spring and fall, and is obviously polluted at all times by the drainage from a number of ranches along its

course. The area is further characterized by the presence of a large number of springs. Five of these, sampled in the winter, gave chloride contents varying from 14.38 to 28.20 parts per million. The average from the three seasons of one of them, graded "C," was 20.77 parts per million.

E. 7—The division E.7 is the one drained by San Antonio, or "Adobe" Creek. The watershed is well protected by Black Mountain from the effect of the trade winds, and the upper part of the stream carries a good flow of water throughout the year. Sampled above any possible source of pollution an average value of 17.23 parts per million was found, and tributaries gave corresponding values for their chloride contents.

E. 8—Subdivision E. 8 consists of the two forks of Permanente Creek and their watersheds. They are both well protected by Black Mountain from the wind and fog. The northern is almost dry except in mid-winter. A tributary stream flowing from a spring well up the side of the mountain gave an average chlorine content of 12.68 parts per million. The southern fork flows the year through unless the summer be exceptionally dry. Above any possible pollution the average chloride content was 16.35 parts per million, with a very small seasonal variation; a tributary of the same character gave 16.29; further down, below a little cultivation, the average was 19.54, and in the valley, below obvious pollution, it was 35.59 parts per million.

E. 9—Stevens Creek, whose watershed is subdivision E. 9, is one of the larger streams on the eastern slope. It rises near the summit of Black Mountain, on the southern side, and near the southern saddle described on page 57 where the division E. 5 was described. The course is at first southeastwards for about three miles. The watershed is formed by a valley between the main ridge, which here has an elevation of about 2500 feet, and Monte Bello ridge. The latter starts at the summit of Black Mountain at an elevation of 2787 feet, but descends to about 1500 feet at a point some three miles to the southeastward. This valley is parallel to, and in line with, the valleys described in division E. 2, E. 3, and E. 5. At the summit it is exposed to wind and fog, but otherwise it is well protected by the main ridge. At a point about three miles southeast of Black Mountain the valley is crossed by Table Mountain (elevation about 2000 feet) and the stream is turned northeastward. After flowing about two miles in this direction, around the end of Monte Bello ridge, the stream reaches the open valley. Beyond this the stream bed is dry from late spring till late fall, but during the winter it runs almost due north to San Francisco Bay.

The headwaters, a tributary at Table Mountain, and the lower stream near the valley were sampled at the three seasons, and fall samples

for chlorides only were taken along the whole course of the stream and from many of its tributaries. For the upper part of the watershed values for the chloride content between 13.82 and 17.70 parts per million were found. In the lower stream, below possible pollution, the content was as high as 25.63 parts per million.

E. 10—The subdivision E. 10 is a small one of little importance. It consists of the area between E. 9 and E. 11, which is drained by a stream, Calabazas Creek, which is dry for the greater part of the year. The mineral springs known as "Azule Springs" are located on the upper part of the watershed. A sample from the creek in the fall, below possible pollution, and just above the point where the stream disappeared, gave 28.58 parts per million of chlorides.

E. 11—The area designated E. 11 is a large one, and consists of the watersheds drained by Campbell Creek and its tributaries. The main ridge (elevation from 3000 to 2500 feet), runs northwest and southeast, the creek almost due northeast from the ridge to the bay. This division, as well as the next two, E. 12 and E. 13, have some of the characteristics of those on the western slope as has been pointed out on page 54. They are much larger than those which have been considered, the watersheds receive a very much larger rainfall, are more heavily wooded, the streams are larger, and except in their lower courses in the valley, flow throughout the year. The watersheds are well protected from the ocean fogs and winds. This protection is afforded by their much greater distance from the ocean, and by the ranges to the west of the main ridge. A storage reservoir located in the mountains on the line between E. 11 and E. 12, gave an average chloride content of 9.44 parts per million with a very low seasonal variation. The streams above possible pollution showed the same small seasonal variation, and gave average values for the chloride content of 13.05, and 10.96, parts per million; below possible pollution the chloride content was about five parts per million greater.

E. 12—The conditions which have been described for subdivision E. 11 apply also to E. 12, the region drained by Los Gatos Creek. In this latter case the area is larger, and the stream flow greater. The watershed is however inhabited, ranches are scattered over the whole area, and no samples from streams classed "A" were obtained. The chlorides in a number of streams graded "B" varied from 10.14 parts per million in the winter to 16.61 in the fall.

E. 13—Subdivision E. 13 is a large area, drained by two forks of the Guadaloupe River. Only the western fork was included in this investigation. The conditions are similar to those described for E. 12, except that the upper part of the watershed is uninhabited and this stream may be

classed "A." Here the average chloride content was 10.25 parts per million, a "C" grade tributary gave on the average 11.99 and the main stream below probable pollution the average of 22.64 parts per million.

W. 1—Subdivision W. 1, on the western slope, is so exposed to sea winds, fogs and spray that the conditions are distinctly abnormal. The distance from the ocean to the ridge is short, the hills are bare, wind-swept pastures. The streams are small, and flow only during the winter. Two streams and two springs were sampled, and the chlorides varied from 41.8 parts per million in the winter to 62.02 parts per million in the fall. The seasonal variation in a stream was twelve, and in a spring was six, parts per million.

W. 2—Subdivision W. 2 is more important, as it consists of the watershed drained by San Pedro Creek and its tributaries. This stream has a fairly large flow the year through, and consequently the seasonal variation in the chloride content is very much smaller.* The watershed is uninhabited, and is protected on the south by a high ridge of mountains (elevation 1000-1500 feet) and on the north by the hills separating it from W. 1. The chloride contents are among the lowest found on the western slope, and range between 21.80 and 28.80 parts per million.

W. 3—In subdivision W. 3 are grouped a number of small independent streams and their watersheds. They are all very much exposed to the ocean winds and fogs; those in the southern rather more so than those in the northern part. The samples showed a somewhat abnormal seasonal variation. The stream at Green Canyon averaged 42.11 parts per million, that at the "Italian ranch" 25.69, a spring at the same place 30.56, and San Vincent Creek, graded "C," 40.96 parts per million.

W. 4—The watershed of Deniston Creek and its tributaries forms the subdivision W. 4. The stream is a large one, but slightly exposed to pollution above the points of collection of the samples by several ranches and irrigating systems. A sample further up the stream was not obtained. At this point, graded "B," the average chloride content was 33.10 parts per million, and the value in the spring was seven parts higher than in the fall.

W. 5—The subdivision W. 5 includes a group of small independent streams and their watersheds. None of them carries any large amount of water. Only one was sampled, and, in the fall, a chloride content of 79.2 parts per million was found. At this time the stream was very low,

* As has been pointed out on page 54, the greater rainfall on the western slope as compared with the eastern, results in a correspondingly smaller seasonal variation throughout the area.

so that the high value may be due to the season, and is probably not normal.

W. 6—The area drained by Frenchman's Creek defines subdivision W. 6. This is a large stream, with a good flow throughout the year. The watershed is rather long and narrow, and is somewhat protected from the ocean winds by the surrounding hills. Sampled at the diverting dam of an irrigating system an average chloride content of 27.27 parts per million, and the small seasonal variation characteristic of the western slope, were found.

W. 7—The watershed of Pilarcitos Creek and its tributaries forms division W. 7. The stream rises in the mountains between E. 3 and W. 4 and W. 6, and is impounded by a dam, forming Pilarcitos Lake. This part of the watershed is exposed to the ocean winds from the northwest. As has been stated on page 55, the water from the lake is run into San Andreas Lake through tunnels and flumes. The average chloride content of the lake water was 19.19, and of a small tributary from the south flowing into the lake through a flume 23.23 parts per million. Below this dam the stream flows through a narrow valley, is fed by numerous small tributary streams and springs, and is impounded again at Stone Dam. Here the water is again diverted into San Andreas Lake. The average chloride content of the water at Stone Dam was 24.21, and of a small tributary spring nearby 29.56 parts per million. Below this the stream flows on through a narrow valley with considerable forest growth to a point northeast of the town of Half Moon Bay, where it turns to the southwest and runs into the ocean. At this turning point the average chloride content was 37.45 parts per million. A tributary stream below this, sampled in the fall and above possible pollution, gave 27.85 parts per million. Another tributary several miles to the south, draining an inhabited valley and graded "D," gave 42.41 parts per million of chlorides in the fall.

W. 8—Subdivision W. 8 is one of the group which contains thick forest growth. It is drained by Purisima Creek and its tributaries. A spring near the ridge, just west of King's Mountain House, showed an average chloride content of 14.02 parts per million. The stream itself, sampled in fall and spring only, gave an average of 28.53, and a small tributary, sampled in the spring, 21.52 parts per million of chlorides. After the inflow of a large tributary somewhat exposed to pollution the chlorides in the main stream were 33.19 parts per million in the fall.

W. 9—The subdivision W. 9 is a small one drained by Lobitos Creek. The watershed is bare pasture land, with little or no forest growth. The chlorides in the fall were 135.5 and in the spring 120.0 parts per million.

These very high values are not sufficiently accounted for by the possibility of slight pollution from one or two ranches, and from the cattle pastures, as other streams draining very similar country do not show any such high chloride contents.

W. 10—The region drained by Tunitas Creek and its tributaries forms subdivision W. 10. Only the main stream, above all possibility of pollution, was sampled; and here the average chloride content was 46.70 parts per million.

W. 11—The subdivision W. 11 is a very large one, and consists of the entire region drained by San Gregorio Creek and its many tributaries. It is for the most part densely wooded with heavy forest growth, is not especially exposed to the ocean winds, and possesses those characteristics which have been described on page 54 in the discussion of the group W. 8 — W. 13. The following data were obtained from samples taken from tributaries. Harrington Creek, sampled winter and spring only, gave an average chloride content of 49.60 parts per million; a small stream tributary to La Honda Creek (three samples), a value of 29.51; La Honda Creek further down, graded "C," 39.62; and Alpine Creek, graded "C," gave 30.15, all expressed in parts per million.

W. 12—No samples were obtained from subdivision W. 12. It consists of a small area drained by Pomponio Creek.

W. 13—The extensive area drained by Pescadero Creek forms subdivision W. 13. This stream is the largest on the western slope, and flows throughout the year. The watershed is very heavily wooded with dense forest growth and has those characteristics of the western slope which have been described on pages 49 and 54. Samples taken from the streams above all possibility of pollution gave an average value of 43.71 parts per million of chlorides. A tributary, Peters Creek, gave the distinctly higher value of 51.16 parts per million. Its watershed is less heavily wooded, and its situation on the western side of the main ridge exposes it to the ocean winds which blow up the valley. About three miles further down the main stream, above any possibility of appreciable pollution, the average chloride content was 38.66 parts per million. At the town of Pescadero, above the main bridge over the stream, the chloride content in the fall was 49.9 parts per million.

The values obtained for the chloride contents have been plotted on the accompanying map of the peninsula. The average of the values obtained at the three seasons has been used. When data for one or two seasons only had been collected, the average value was estimated, on the basis of the seasonal variation at neighboring points. These estimated values are given in round numbers, and are enclosed in parentheses on the

map. Curves, "isochlors," were then drawn through the points of equal chloride content. With the exception of a few springs, and two streams, these curves indicate the normal chloride values very satisfactorily. Six samples from streams, evidently polluted, or obviously affected by some abnormal condition, were omitted altogether.

The map brings out clearly the remarkably large variation in the normal chloride content within a comparatively short distance. Two important factors are emphasized, namely rainfall and sea winds.

The resemblance between the paths of the lines of equal chloride content and of equal rainfall is striking. The region about Lake Pilarcitos, which has the restrictedly high rainfall of fifty inches, has the lowest chloride content within fifteen miles. San Pedro Creek, which drains this region on the north, has the lowest chloride content found on the western slope. Southwards, where the rainfall decreases, the chlorides increase, until another region of high rainfall is encountered. Here, again, the chloride content decreases. In the southern district the lines of equal chloride content do not coincide so closely with those of equal rainfall as they do in the northern region. This may be due to two causes: First, the sheltering effect of the mountains, which would tend to displace the low value "isochlors" to the eastward; and, second, incomplete data. The region to the south and southwest of Black Mountain is uninhabited and not easily accessible. When data is this district have been obtained the low "isochlors" may be deflected more to the southwest, towards the point of maximum rainfall.

Superimposed on this rainfall factor is that of the sea winds. The effect of this latter is both general and local. The general effect is seen in the difference between the lowest chloride contents in the regions of highest rainfall. Around Lake Pilarcitos, rainfall fifty inches, the lowest chloride found was nineteen parts per million; around Black Mountain, rainfall thirty-five inches, the lowest is fourteen parts per million, and south of Los Gatos, rainfall about forty inches, the lowest is ten parts per million. This general decrease in the chloride content from north to south may be considered to be the result of the more complete shelter from the sea winds afforded by the main ridge.

This "sea-wind" factor is especially prominent locally at the following points. In the San Pedro Valley the "isochlors" are deflected to the southeast, against increasing rainfall; here the sea winds sweep up the valley with unchecked force. North of San Andreas Lake, division E. 1, the "isochlors" are deflected away from the ocean. This region is especially exposed to the ocean winds and spray. In the valley west of Half Moon Bay the "isochlors" recede from the ocean; here again the ocean

winds sweep up the valley and over the pass described in considering division E. 3. The same effect is noticed in the San Gregorio Valley, and its absence is marked in the case of the Pescadero Valley where a high range to the north affords protection. On the eastern side an instance is seen at the head of Corte Madera Creek, northwest of Black Mountain. This is at the "southern pass" described on page 57, division E. 5, and the marked deflection of the "isochlors" is apparent.

A little further north a pinching together of the two sides of the twenty parts per million "isochlor" at the point of the lowest, middle pass of division E. 5 is apparent. South of this the general protection afforded by the main ridge eliminates any local effect.

It will be interesting to note whether, as work of this character is extended to larger regions along the Pacific coast, the general influence of the rainfall, and the general as well as local influence of the sea winds, retain the position of prime importance which is indicated by this investigation.

Hardness.

As a class all the waters sampled were very hard. This is not a local peculiarity, but is generally true of all the waters of the Western states.

The total hardness varied irregularly with the seasons, but was often highest in the fall, lowest in the winter, and intermediate in the spring. On the eastern slope the total hardness was generally between two hundred and two hundred and fifty parts per million (expressed in terms of calcium carbonate), for streams, and between fifty and one hundred and twenty for reservoirs. On the northern part of the western slope the total hardness was less, sometimes as low as thirty parts per million, but increased in the southern part to about the same values as on the eastern side. The springs were generally low in total hardness. The temporary hardness likewise varied greatly. The general range for streams was from one hundred and fifty to two hundred and fifty parts per million (expressed in terms of calcium carbonate); it was lower in reservoirs (40-120), lower in the streams on the northern part of the western slope, and lower in springs. The permanent hardness ranged in general from twenty to fifty. It was lower in the reservoirs, higher in the streams on the northern part of the western slope, and higher in the springs. Free alkaline carbonates appeared in waters from different sources at irregular intervals. The amount seldom exceeded thirty parts per million.

Total Solids.

The total solids were on the whole high. In streams the value was

generally between two hundred and three hundred parts per million. Those in the southern part of the western slope gave as high as four hundred to five hundred parts per million. Springs and reservoirs were generally between one hundred and two hundred parts per million. The high values for total solids as well as for hardness, as compared with Eastern waters, are due to the influence of the same factors that bring about the high chlorides, namely the smaller rainfall, and the long summer period of weathering with little washing away of the resulting materials.

WELLS.

Samples were collected from fifteen deep wells on the floor of the Santa Clara Valley. These are typical of the large number which provide the water supply of this relatively thickly populated region. They all lie in a belt which follows the shore of the bay and are from one hundred yards to two miles distant from the marsh line. All are bored and cased wells of considerable depth, that is from one hundred to five hundred feet. They are abundantly supplied from underground sources, but their relation to the streams of the peninsula is as yet somewhat uncertain. The wells are "artesian" in the sense that, if not drawn upon too heavily, the water flows out of the top of the boring with considerable force. The data obtained are not considered sufficient to warrant the drawing of any important conclusions, and it is the intention of the writer to extend this work in this direction in the future. The results are summarized in the following paragraphs.

Many of the wells contain large amounts of free ammonia. The values obtained varied from none to 0.228 parts per million. The albuminoid ammonia results were lower, varying from none to 0.080 parts per million. No fixed relation between the two ammonias could be observed, nor did the absence of the one coincide with the presence or absence of the other. Nitrites were generally absent, and not often over 0.005 parts per million. One well, from which five samples extending over one year were taken, gave an average of 0.021 parts per million. Their presence at all seasons seemed characteristic of certain wells, and their absence of others. Nitrates were generally absent, but appeared regularly in certain wells. The amount was generally below 0.50 parts per million, the maximum was 1.40 parts per million. The chloride content varied widely, the range being from fifteen to two hundred and fifty-eight parts per million. Omitting the three highest values the range was from fifteen to forty parts per million. As pollution seems out of the question in wells of this class the explanation of the high chloride content must be sought in

either the source of the water, if it can be determined, seepage through marine deposits, or infiltration of salt water from the bay. The wells in the southern part of the field showed the lowest chloride contents; with an average of between fifteen and twenty parts per million.

The water from most of the wells was very hard, the total hardness being generally about two hundred parts per million, and the temporary only a little less. The highest permanent hardness was 25.3 parts per million. Free alkaline carbonates were common (found in fifteen out of twenty-five samples analyzed) and were generally between forty and seventy parts per million. Well No. 12 was abnormal and contained: temporary hardness 77.2, free alkaline carbonates 146.0 parts per million expressed in terms of calcium carbonate. The total solids were high, ranging from 264 to 688 parts per million.

The seasonal variation was apparent, but small. The free and albuminoid ammonia, and nitrites, varied irregularly. The nitrates, in those wells which always contained a small amount, were highest in the winter. The chlorides decreased in the winter to about two parts per million below the fall values, and increased a corresponding amount in the spring. The total and temporary hardness generally increased a little during the winter months, while the permanent hardness and free alkaline carbonates fluctuated irregularly. In the winter the total solids were a little higher than during the fall and spring.

SUMMARY.

The object of this investigation is to determine the normal constituents of the potable water of the San Francisco peninsula, from a sanitary point of view, and before the growth in the population affects too seriously the natural purity of the water supplies. The significant constituents, and the interpretation of water analyses, are discussed briefly. The area studied included approximately six hundred and seventy-five square miles lying south of Baden station on both sides of the peninsula. This was divided into twenty-six subdivisions, thirteen on each side. The characteristic topographical and climatological features of the region are described in detail. Especial emphasis is laid on the distribution of the rainfall, the presence of the strong ocean "trade winds," both of which are peculiarly characteristic of the Pacific coast of California, and on the resulting, very marked, seasonal variation in the constituents of all the waters.

A careful, personal, survey was made of each watershed, and the points of collection were chosen with especial regard to the importance of

obtaining as nearly unpolluted water as possible. The sources sampled were classified in the field according to their probable purity. The sampling and the analytical work were done by the writer personally in accordance with the standard methods in general use. Since the usual phenol sulphonic acid method for the determination of nitrates was known to be unsatisfactory in the presence of large amounts of chlorides, a special study of the methods available for this determination was undertaken.

The detailed results of this study of the availability of the phenol sulphonic acid method, of the reduction method, and of their relative efficiency are given, and lead to the following conclusion. "For waters containing large amounts of chlorides the nitrogen present as nitrate may best be determined by the 'reduction method,' using the copper-zinc couple and oxalic acid. If the result of the determination indicates a nitrogen content in excess of five parts per million, the determination should be repeated, using the phenol sulphonic acid method, and standards prepared according to Mason's suggestion." With low nitrates the error may be as much as ten per cent, with twenty parts per million or over the error should not exceed three per cent.

The analytical data obtained from two hundred and forty samples are given in a table. These samples were taken from one hundred and twenty-six points of collection, from fifty-three of which at least three samples at the three characteristic seasons of the year, namely fall, winter, and spring, were collected. Of these samples one hundred and three were analyzed for chlorides only. In addition thirty-three samples were collected from fifteen deep wells, of which eight were analyzed for chlorides only. A map is given, on which are shown the several watersheds, the subdivision numbers, the points of collection, and the laboratory number of a sample from each point of collection. The analytical results obtained for each constituent are considered separately.

The turbidity, sediment, color, odor, and change of residue on ignition are found to be of minor importance in dealing with this class of waters, and without influence on the more important constituents.

The free and albuminoid ammonias varied both in quantity and in type of seasonal variation with the character of the vegetation on the watersheds. The extreme values at any season or on any watershed that should be passed without suspicion are set for free ammonia at 0.050 and for albuminoid ammonia at 0.160 parts per million in the case of streams. For clean reservoirs the limits are 0.030 for free, and 0.150 for albuminoid, ammonia. The data for springs are not conclusive.

Nitrites were generally absent, especially in the fall and spring

months. The maximum values, in the winter are, for streams 0.003, and for reservoirs 0.006 parts per million. The small number of springs examined did not afford conclusive data. Only small amounts of nitrates were found in any but exceptional waters. The normal values for streams are, in the fall, none, to 0.15, in the winter and spring a trace to 0.75 parts per million. The data for reservoirs lead to the same conclusions, and for springs are not conclusive.

The chlorides were determined with especial care, and the results obtained in each subdivision are treated separately, and the influence of local conditions is emphasized. Samples were collected from one hundred and twenty-six points of collection. From fifty-three of these points at least three samples at the three characteristic seasons of the year, namely, fall, winter and spring, were taken. The results show the exceedingly high chloride content of these waters as compared with those of the Eastern states. The normal values ranged, according to geographical location, from ten to fifty parts per million. This high chloride content is characteristic of the waters of the Pacific coast, and is due to the influence of two factors, namely the rainfall and the ocean winds. The rainfall is in general much less than that of the Eastern states, is almost entirely confined to the winter months, and leaves a long summer period with practically no rainfall, and consequently no washing or rinsing of the ground. The ocean winds are far greater in force and frequency than any met with in the Eastern states. The "trade winds" blow over the ocean from the northwest day after day, with clock-like regularity, throughout the summer months, and with considerable violence. The regularity and force of these winds is shown by the marked bending towards the southeast of the oak trees growing in the more exposed places. These winds carry to the land ocean fogs, and large amounts of salt in the form of impalpable dust, the product of the evaporation of the spray thrown into the air by the "white-caps" and the long, unbroken line of heavy surf. The results of the analyses were mapped, and "isochlors" were drawn. These curves coincide satisfactorily with the data collected, and show clearly the general influence of the variation in rainfall, and the general as well as the local influence of exposure to the sea winds. The seasonal variation was found to be great, and to vary with local conditions. The highest values occur in the fall, the lowest in the winter, and the intermediate in the spring.

The waters were all very hard; as much as two hundred and fifty parts per million in streams and one hundred and fifty in reservoirs was not uncommon. The temporary hardness varied from one hundred and fifty to two hundred and fifty parts per million in streams and from

forty to one hundred and twenty in reservoirs. The permanent hardness was lower, seldom over fifty parts per million in streams, and less in reservoirs. Free alkaline carbonates appeared in all classes of waters at varying seasons, but the amount rarely exceeded thirty parts per million. The total solids ranged between two hundred and four hundred parts per million in the streams, and between one hundred and two hundred in the reservoirs. The springs were between the limits for streams and reservoirs. These high values are due, as has been pointed out in the case of the chlorides, to the relatively small rainfall, and long rainless summer period of weathering without any washing of the surface of the ground.

The data on the wells are discussed separately, and are considered to be inadequate. It is hoped to supplement them in the future. Fifteen typical wells were taken from the "well belt" which borders the southern shores of San Francisco Bay. As a class they showed high free ammonia (maximum 0.228 parts per million) lower albuminoid ammonia, absence of any fixed relation between the two, and irregular seasonal variation. Nitrites and nitrates were generally absent, but always present in certain particular wells in amounts as large as 0.021 parts per million of nitrites and 1.40 of nitrates. The chlorides varied over as large a range as did those for the streams. The average in the southern part of the district was between fifteen and twenty parts per million, and increased in the northern. The hardness and total solids were about the same as for the streams. The seasonal variation of all the constituents was less marked in the wells than in the streams.

This investigation was undertaken at the suggestion, and was carried out under the inspiration and direction, of Dr. John M. Stillman, Professor of Chemistry at this University.

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